

## Electronic Excitation in Air and Carbon Dioxide Gas

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### **ABSTRACT**

*This lecture presents review of elementary processes in nonequilibrium low-temperature plasma of chemical compositions (air and carbon dioxide mixtures) frequently occurring in different aerospace applications. The general attention is given to electronic kinetics of atoms and diatomic molecules in the frame of radiative collisional model (Chapters 4 and 5).*

*The thermodynamic models of the plasma are considered in the Chapter 2. The place of the radiative-collisional model among other models is defined in the chapter.*

*Formulation of the generalized radiative-collisional model is given in Chapter 3.*

*The sixth chapter of the lecture presents the problem of data processing automation. This problem is considered on the example of prediction of oscillator strengths of atomic species.*

*Spectral emissivity of strong shock waves in air and carbon dioxide mixtures is analysed in Chapter 7. The hybrid thermodynamic model, including the local thermodynamic equilibrium and the radiative-collision models, is formulated and used in the chapter. Numerical simulations and comparison with available experimental data are presented there.*

*The Chapter 7 contains detailed description of kinetic data which were used by the author at consideration of physical and chemical kinetics in strong shock waves. The last part of the Chapter 7 contains short review of some other kinetic models.*

*The text of the lecture contains an appendix. Some kinetic data which can be used at creation of various kinetic models are presented in the appendix. All of these data were used by the author at solution of concrete problems of radiation gas dynamics, therefore from the author's point of view, these can be recommended for practical work in aerospace aerophysics.*

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## 1.0 INTRODUCTION

Electronic kinetics of atomic and molecular components of gases and plasma is of considerable interest to aerophysics, non-equilibrium physics and chemistry of plasma, physics of lasers. Of particular interest is the electronic kinetics in strong shock waves and gas discharges [1–6].

Recall the general characteristics of plasma in a variety of conditions [6–8].

1. The macroscopic characteristics:

- The Debye radius

$$r_D = \sqrt{\frac{kT_e}{8\pi n_e e^2}} = 4.86 \sqrt{\frac{T_e, [\text{K}]}{n_e}} = 525 \sqrt{\frac{T_e, [\text{eV}]}{n_e}}, \text{ cm.}$$

The Debye radius gives spatial scale for macroscopic description of plasma.

- The plasma frequency

$$\omega_p = \sqrt{\frac{4\pi e^2 n_e}{m_e}} = 5.65 \times 10^4 \sqrt{n_e}, \text{ s}^{-1}$$

Characteristic time  $\tau_p = \omega_p^{-1}$  should not be exceeded by characteristic time of any microscopic interaction in plasma.

2. The microscopic characteristics:

- The averaged velocity of electrons at Local Thermodynamic Equilibrium (LTE) conditions

$$v_e = \sqrt{\frac{8kT}{\pi m_e}} = 6.21 \times 10^5 \sqrt{T_{[\text{K}]}} = 6.71 \times 10^7 \sqrt{T_{[\text{eV}]}} , \text{ cm/s,}$$

and averaged velocity of heavy particle of mass  $m$

$$v = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8kT}{\pi M_0 A}} = 1.45 \times 10^4 \sqrt{\frac{T_{[\text{K}]}}{A}} = 1.56 \times 10^6 \sqrt{\frac{T_{[\text{eV}]}}{A}} , \text{ cm/s,}$$

where  $A$  is the atomic number of the particle.

- The number of particles in volume of the Debye sphere

$$n_D = (4/3)\pi r_D^3 n,$$

where  $n$  is the volume concentration of the particles, that is the number of particles in  $1 \text{ cm}^3$ .

If  $n_D \gg 1$ , then the continuum approximation can be used for description of the plasma.

Note that such a microscopic characteristics as average electronic velocity is expressed by the macroscopic characteristics:

$$(\omega_p \cdot r_D)^2 = \frac{4\pi e^2 n_e}{m_e} \frac{kT_e}{8\pi n_e e^2} = \frac{kT_e}{2m_e} = v_e^2.$$

It means a plasma particle can move over one Debye radius is one period of plasma oscillation.

Figure 1.1 shows regions of electronic concentrations and temperature in the field of plasma existence.

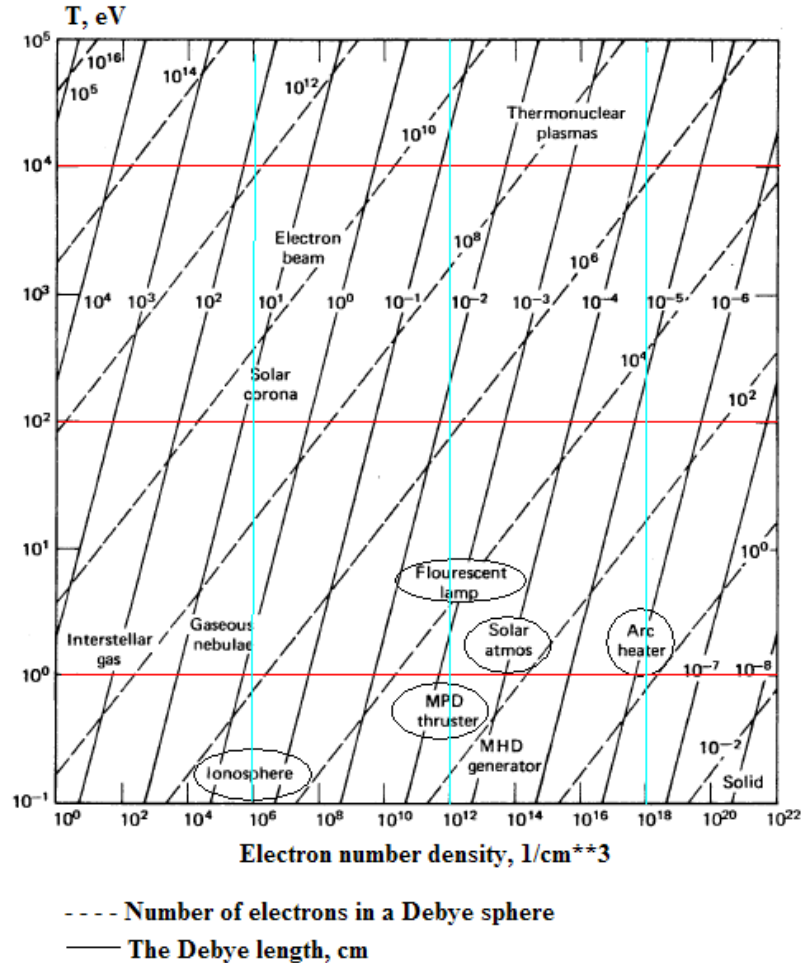


Figure 1.1: Diagram of plasma parameters for different applications (see [6])

Analysis of processes of electronic kinetics, as applied to strong shock wave and gas discharges, are presented in the lecture. These are two fundamentally different objects of application of electronic kinetics.

Electrons and heavy particles are heated in shock waves due to collision processes. Other mechanisms of the particles heating is observed in gas discharge plasma. Electrons in gas discharges are heated due to interaction with external electric field, and then they warm heavy particles by collisions. The term “electronic kinetics” will be used in the lecture for analyses of energy of free electrons and of heavy particles on internal electronic degrees of freedom

The foundation of the processes of electronic kinetics is based on Refs. [1,6,7,9–13].

## 2.0 THERMODYNAMIC MODELS OF PLASMA

### 2.1. The Local Thermodynamic Equilibrium (LTE) model

The full thermodynamic equilibrium is characterized by the Maxwellian distribution of particles on velocities. For example, for electrons

$$dn_v = 4\pi n_e \sqrt{\left(\frac{m_e}{2\pi k T_e}\right)^3} e^{-(m_e v^2 / 2k T_e)} v^2 dv, \quad (1)$$

where  $n_e$  is the electron concentration ( $\text{cm}^{-3}$ ). Temperature of electrons  $T_e$ , ions  $T_i$ , and neutral particles  $T_n$  equal between them:  $T_e = T_i = T_n$ .

The Boltzmann formula describes distribution of atoms, ions and molecules on internal electronic states:

$$\frac{n(u)}{n(l)} = \frac{g(u)}{g(l)} e^{-\frac{E_u - E_l}{k T_e}}, \quad (2)$$

where  $E_u, E_l$  are the energies of upper and low bound states;  $g_u, g_l$  are the statistical weights of the upper and, lower bound states.

The Saha equation gives distribution of heavy particles on degree of ionization:

$$\frac{n_z n_e}{n_{z-1}} = \frac{2g_z}{g_{z-1}} \left( \frac{2\pi m_e k T_e}{h^2} \right)^{3/2} e^{-\frac{I}{k T_e}}, \quad (3)$$

where  $I$  is the potential of ionization for atom ( $z=1$ ) or ion ( $z \geq 2$ ) from the ground state. It is assumed that condition  $z=1$  corresponds to neutral particle.

Volume density of heat radiation in equilibrium conditions is given by the Planck law:

$$U_\lambda = \frac{8\pi h c}{\lambda^5} \frac{1}{e^{hc/\lambda k T} - 1}, \quad (4)$$

where  $U_\lambda$  is the spectral volume density of heat radiation in spectral region from  $\lambda$  up to  $(\lambda + d\lambda)$ . Unfortunately, plasma of shock waves and electric discharges as a rule is not optical thick. Therefore the plasma emits of heat radiation differently than (4).

It is agreed that the plasma is in Local Thermodynamic Equilibrium if conditions (1)–(3) are satisfied, and the condition (4) is not satisfied [14]. Description of several variants of LTE is also presented in [15].

### 2.2. Model of the Partial Local Thermodynamic Equilibrium (PLTE)

This model was considered in Refs. [16, 17]. It is agreed that the plasma is in partial local thermodynamic equilibrium if population of excited states  $j > j^*$  can be described by the Saha equation. Another words, there are conditions in the plasma for introduction of a unified electronic temperature for free electrons

and excited electronic states, although such a temperature can not be used for prediction of population of ground states.

### 2.3 Coronal plasma model

Let us consider simple two-level model of atomic plasma:



where  $A^*$  is the excited atom.

Equation (1) describes excitation of atom  $A$  at collision with particle  $B$  (for example, with electron). Process (2) is the deexcitation of  $A^*$  with emission of photon. It is possible to unite two processes (1) and (2) into unified kinetic scheme

$$\frac{d[A^*]}{dt} = k_f [A][B] - k_r [A^*][B] - \frac{[A^*]}{\tau_{rad}}. \quad (3)$$

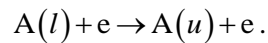
At steady-state conditions

$$k_f [A][B] = [A^*] \left( k_r [B] + \frac{1}{\tau_{rad}} \right). \quad (4)$$

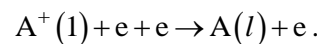
It is agreed that the plasma coronal model is realized, if  $\frac{1}{\tau_{rad}} \ll k_r [B]$ . In this case the population of the excited states is defined by the velocity of their radiative decay.

### 2.4 Radiative-Collisional (RC) model

Most likely the RC model was firstly considered in Refs. [18]. In the first RC model only two collision processes were taken into account. The first one is the excitation of atoms by collisions with electrons:



The second one is the three-body recombination:



In modern practice, the RC models include as much as possible equations for states populations (state-by-state approach) with detail description of radiative processes.



### 3.0 CLASSIFICATION OF ELEMENTARY PROCESSES INCLUDING INTO RC MODELS [8]

#### 3.1 Ionization at collision of atoms and molecules with electrons

Kinetic scheme of this process is expressed as follows:



where  $A^{(z-1)}(n)$  is the atom, molecule or ion with the degree of ionization  $(z-1)$  ( $z=1$  is the neutral particle) in quantum state  $n$ ;  $A^{(z)}(1)$  is the ion with the degree of ionization  $z$  at ground state.

Kinetic equation of the process (1) velocity is formulated as follows:

$$\frac{d[A^{(z-1)}]}{dt} = -k_i^{(e)}[A^{(z-1)}][e], \quad (2)$$

where  $[A^{(z-1)}], [e]$  are the concentration of particles and electrons;  $k_i^{(e)}$  is the rate coefficient of collisional ionization.

If it is granted that colliding particles are distributed with Maxwellian function, then

$$k_i^{(e)} = \langle v \rangle \int_0^\infty \sigma(n) e^{-(E/kT)} \left( \frac{E}{kT} \right) d\left( \frac{E}{kT} \right), \quad (3)$$

where  $\sigma(n)$  is the cross section of ionization from quantum state  $n$ . In the general case  $n$  identifies the full list of quantum numbers.

Cross section of ionization of the  $n$ -th state of hydrogen atom is defined as follows (here and further all estimations will correspond to hydrogen atoms):

$$\sigma(n) = 4\pi a_0^2 \left( \frac{I_1^H}{I_n} \right)^2 f_n \xi_n \frac{U_n - 1}{U_n^2} \ln(1.25 \beta_n U_n), \quad (4)$$

where  $U_n = \frac{E_e}{E_n}$ ,  $E_e = \frac{m_e v_e^2}{2}$ ,  $E_n = z^2 \frac{I_1^H}{n^2}$ ,  $\beta_n = 1 + \frac{z-1}{z+1}$ ,  $I_1^H = 13.59$  eV;  $\xi_n$  is the number of equivalent electrons at the  $n$ -th state ( $\xi_n = 1$  for hydrogen);  $f_n$  is the oscillator strength for ionization from state  $n$  attributed to one electron ( $f_1 = 0.66$ ,  $f_2 = 0.71$ ,  $f_3 = 0.81$ ,  $f_4 = 0.94$ ,  $f_{n>5} = 1$ );  $E_n$  is the energy of ionization from state  $n$ .

If one takes into account (4), then the rate coefficient of ionization is calculated as follows:

$$k_i^{(e)} = 4\pi a_0^2 \left( \frac{I_1^H}{I_n} \right)^2 f_n \xi_n \sqrt{\frac{8kT_e}{\pi m_e}} u_n \Psi_1(u_n, \beta_n), \quad (5)$$

where

$$u_n = \frac{E_n}{kT_e}, \quad \Psi_1(u_n, \beta_n) = \int_{u=x}^{\infty} \left[ \left( 1 - \frac{x}{u} \right) e^{-u} \ln \frac{1.25\beta u}{x} \right] du.$$

Function  $\Psi_1$  is the quantum correction for atoms.

### 3.2 Recombination at the three-body collision with electron

Kinetic scheme of this process is expressed as follows:



Kinetic equation of the process (6) velocity is formulated as follows:

$$\frac{d[A_n^{(z-1)}]}{dt} = k_r^{(e)} [A^{(z)}(1)] \cdot [e]^2, \quad (7)$$

where  $k_r^{(e)}$  is the coefficient of rate of recombination.

The principle of detailed balancing allows calculate of the rate coefficient through the rate of ionization

$$k_r^{(e)} = \frac{g_n}{2g_z} \frac{1}{Q_e} k_i^{(e)} e^{u_n}, \quad (8)$$

where  $g_n$  is the statistical weight of the state  $n$ ;  $n$  is the principal quantum number;  $g_n = 2n^2$  for hydrogenic ions;  $g_z$  is the statistical weight of ground state of ion ( $g_z = 1$  for the proton); coefficient “2” takes into account the degeneracy on electron spin ( $+\frac{1}{2}$  и  $-\frac{1}{2}$ );

$$Q_e = \frac{(2\pi m_e kT_e)^{3/2}}{h^3} \quad (9)$$

is the partition function of translational motion of electrons.

### 3.3 Radiative recombination of ions

Kinetic scheme of this process is expressed as follows:



where  $h\nu$  is the electromagnetic field quantum.

Kinetic equation of the process (10) velocity is formulated as follows:

$$\frac{d[A_n]}{dt} = \beta_{r,n} [A^{(z)}(1)] \cdot [e], \quad (11)$$

where  $\beta_{r,n}$  is the rate coefficient of the radiative recombination:

$$\beta_{r,n} = 5.20 \times 10^{-14} z u_1^{3/2} G_n n^{-3} [-E_i(u_n)] e^{u_n}, \quad (12)$$

$G_n$  – is the Gaunt coefficient ( $G_1 = 0.8$ ;  $G_{n>1} = 1.0$ );

$$-E_i(-x) = \int_x^\infty \frac{e^{-t}}{t} dt = \begin{cases} \frac{e^{-x}}{x}, & x > 5; \\ \ln\left(\frac{1}{x}\right) - C, & x < 0.2; \end{cases} \quad (13)$$

$$C = \lim \left[ \sum_{k=1}^n \left( \frac{1}{k} \right) - \ln n \right] \text{ is the Euler constant.}$$

### 3.4 Photoionization from state $n$

Kinetic scheme of this process is expressed as follows:



Kinetic equation of the process (14) velocity is formulated as follows:

$$\frac{d[A_n]}{dt} = -\sigma_{i,n} [A_n] \cdot U_v, \quad (15)$$

where  $\sigma_{i,n}$  is the coefficient of photoionization.

For the photoionization from the  $n$ -th state there is the following estimation:

$$\sigma_{i,n} \cong \frac{16}{\sqrt{3}} \frac{\sigma_0}{\alpha^3 c^2} \frac{\xi_n n v_n^3}{z^2} [-E_i(u_n)], \quad (16)$$

where  $\sigma_0$  is the cross section of the Thomson scattering:

$$\sigma_0 = \frac{8\pi}{3} \left( \frac{e^2}{mc^2} \right)^2;$$

$$\alpha = \frac{1}{137} \text{ – is the fine structure constant; } u_n = z^2 \frac{I_1^H}{n^2 kT}.$$

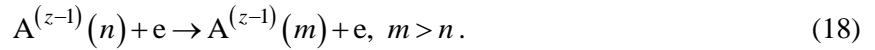
To determine volume density of radiation  $U_v$  one has to solve radiation transfer equation for given plasma configuration. To avoid it the following approximation is used:

$$\frac{d[A_n]}{dt} = -\sigma_{i,n}[A_n] \cdot [e](1 - \chi_{i,n}), \quad (17)$$

where  $\chi_{i,n}$  is the transmission factor. At  $\chi_{i,n} = 1$  plasma is transparent, and photoionization is absent. At  $\chi_{i,n} = 0$  plasma is opaque, and photoionization plays significant role.

### 3.5 Electronic excitation of heavy particles from state $n$

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = -k_{ex}^{(e)}(A, n; E_e | A, m)[A_n] \cdot [e]. \quad (19)$$

For Maxwellian distribution of the particles

$$k_{ex}^{(e)}(A, n; E_e | A, m) = \sigma(A, n; E | A, m) \langle v_e \rangle_{m>n} = 8.69 \times 10^{-8} f_{n,m} \frac{u_1^{3/2}}{z^3 u_{n,m}} \begin{cases} \Psi_1(\beta_{n,m}, u_{n,m}) & \text{for atoms;} \\ \Psi_2(\beta_{n,m}, u_{n,m}) & \text{for ions,} \end{cases} \quad (20)$$

where functions  $\Psi_1$  and  $\Psi_2$  are defined in [9];  $f_{n,m}$  is the oscillator strength of the quantum transition ( $n \rightarrow m$ ).

### 3.6 Electronic deactivation of excited particles at transition $m \rightarrow n$

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = +k_{de}^{(e)}(A, m; E_e | A, n)[A_m] \cdot [e]. \quad (22)$$

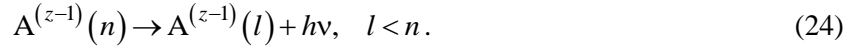
According to the principle of detailed balancing, one can obtain correlation between rates of electronic excitation and de-excitation:

$$k_{de}^{(e)}(A, n; E_e) = \frac{g_m}{g_n} k_{ex}^{(e)}(A, m; E | A, n) e^{u_{n,m}}, \quad (23)$$

where  $u_{n,m} = \frac{E_m - E_n}{kT_e}$ .

### 3.7 Spontaneous radiative depletion of state $n$

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = -\tilde{A}_{n,l}(A, n | A, l, h\nu)[A_n]. \quad (25)$$

Rate coefficients of the spontaneous radiative depletion is estimated as follows:

$$\tilde{A}_{n,l} = \tilde{A}_{n,l}(A, n | A, l, h\nu) = 0.667 \frac{g_l}{g_n \lambda^2} f_{l,n}, \quad (26)$$

where  $f_{l,n}$  is the oscillator strength in absorption;  $\tilde{A}_{n,l}$  is the Einstein coefficient of spontaneous emission.

### 3.8 Photoexcitation from state $l$ to state $n$

Kinetic scheme of this process is expressed as follows:



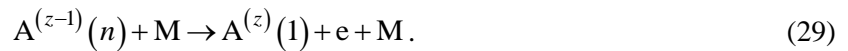
Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = \tilde{B}_{l,n} U_\nu, \quad (28)$$

where  $U_\nu$  is the volume density of spectral radiative energy;  $\tilde{B}_{l,n}$  is the Einstein coefficient. As, before, coefficient of reabsorption  $(1 - \chi_{n,l})$  is introduced to avoid the radiation transfer equation. If  $\chi_{n,l} \ll 1$ , then the volume is optically thick, and at  $\chi_{n,l} \rightarrow 1$  the volume is optically thin.

### 3.9 Ionization of particle $A^{(z-1)}(n)$ at collision with another heavy particle $M$

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = -k_i^{(M)} \left( A^{(z-1)}, n; M | A^{(z)}, 1; e, M \right) [A_n^{(z-1)}] \cdot [M]. \quad (30)$$

Rate coefficient of such an ionization can be estimated at Maxwellian distribution of the particles by the following formula:

$$\begin{aligned}
 k_i^{(M)} &= k_i^{(M)} \left( A^{(z-1)}, n; M \middle| A^{(z)}, 1; e, M \right) = \sigma_{n,M} \langle v_M \rangle = \\
 &= 32\pi a_0^2 \left( \frac{I_1^H}{I_n} \right)^2 f_p \xi_p \left( \frac{kT_B}{\pi m_B} \right)^{1/2} \frac{m_e m_B}{m_H (m_B + m_e)} \Psi_{m_B}(w_n),
 \end{aligned} \quad (31)$$

where  $T$  is the temperature of the heavy particles;

$$\omega_n = \frac{I_n}{kT} = \frac{z^2 I_1^H}{kT \cdot n^2}; \quad (32)$$

$$\Psi_{m_B}(x) \approx \left( 1 + \frac{2}{x} \right) \left\{ \frac{1}{1 + \left[ \frac{2m_e}{(m_B + m_e)x} \right]^2} \right\} e^{-x}. \quad (33)$$

Cross section of the ionization process is expressed in the form

$$\sigma_{n,M} = 4\pi a_0^2 \left( \frac{I_1^H}{I_n} \right)^2 \frac{m_M}{m_H} f_n \xi_n \frac{2m_e}{m_M + m_e} \frac{W_n - 1}{\left[ 1 + \frac{2m_e}{m_M + m_e} (W_n - 1) \right]^2}, \quad (34)$$

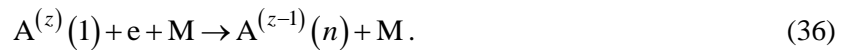
where  $W_n$  is the reduced kinetic energy:

$$W_n = \frac{E_M - E_n}{E_n}, \quad E_M = \frac{m_M v_M^2}{2}, \quad (35)$$

where  $m_M, m_n, m_H, m_e$  are the masses of particles M, A, hydrogen and electron;  $f_n$  is the oscillator strength for ionization from state  $n$  counting on one electron ( $f_1 = 0.66$ ,  $f_2 = 0.71$ ,  $f_3 = 0.81$ ,  $f_4 = 0.94$ ,  $f_{n \geq 5} = 1$ );  $\xi_n$  is the number of equivalent electrons at state  $n$ .

### 3.10 Recombination at three-body collisions with heavy particle

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = -k_r^{(M)} \left( A^{(z)}; e; M \middle| A, n; M \right) [A^{(z)}] [M] [e]. \quad (37)$$

Rate coefficient for recombination at three-body collision with hydrogen atom ( $M \equiv H$ )

$$k_r^- = k_r^{(M)} \left( A^{(z)}; e; M \middle| A, n; M \right) =$$

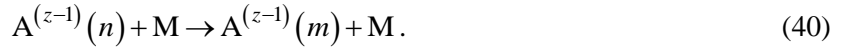
$$= \frac{g_n}{2g_z} \left( \frac{m_M + m_e}{m_M m_e} \right)^{3/2} \frac{n^3}{(2\pi k)^{3/2}} k_f^{(i)} \frac{1}{T^{1/2} T_e} \exp(-u_n + 2u_n^{1/2} w_n^{1/2}). \quad (38)$$

Because  $k_f^{(i)}$  is proportional to  $e^{-w_n}$ , then at  $T_M = T_e$  the common exponential factor in  $k_f^-$  equal to

$$\exp(-w_n - u_n + 2u_n^{1/2} w_n^{1/2}) = 1. \quad (39)$$

### 3.11 Excitation of state $n$ at collision with heavy particle

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_m]}{dt} = k_{ex}^{(M)}(A; n; M | A, m; M) [A_n] [M], \quad m > n. \quad (41)$$

By analogy with ionization process one can write

$$k_{ex}^{(M)}(n, m) = \sigma_{n,m} \langle v_m \rangle = 32\pi a_0^2 \left( \frac{I_1^H}{I_{n,m}} \right) f_{n,m} \left( \frac{kT}{\pi m_M} \right)^{1/2} \frac{m_M m_e}{m_H (m_M + m_e)} \Psi_{m_M}(w_{n,m}), \quad (42)$$

where  $w_{n,m} = \frac{|E_m - E_n|}{kT}$ ;  $f_{n,m}$  is the oscillator strength for quantum jump ( $n \rightarrow m$ ).

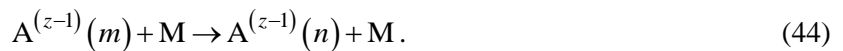
Cross section of this process is

$$\sigma_{n,m} = 4\pi a_0^2 \left( \frac{I_1^H}{I_m - I_n} \right)^2 f_{n,m} \frac{2m_M m_e}{m_H (m_M + m_e)} \frac{W_{n,m} - 1}{\left[ 1 + \frac{2m_M}{m_M + m_e} (W_{n,m} - 1) \right]^2}, \quad (43)$$

$$W_{n,m} = \frac{E_M - |E_m - E_n|}{|E_m - E_n|}.$$

### 3.12 Deactivation of heavy particle from state $m$

Kinetic scheme of this process is expressed as follows:



Kinetic equation for the velocity of the process is formulated in the following form:

$$\frac{d[A_n]}{dt} = k_{de}^{(M)}(m, n) [A_m] \cdot [M]. \quad (45)$$

According to the principle of detailed balancing, one can derive

$$k_{de}^{(M)}(m, n) = \sigma_{m,n} \langle v_M \rangle = \frac{g_n}{g_m} k_{ex}^{(M)}(n, m) e^{-w_{m,n}}. \quad (46)$$

### 3.13 The fundamental equation of collisional-radiative kinetics of quantum states of homogeneous atomic-molecular plasma. The Master equation

The kinetics of filling and deactivation of some quantum level of internal energy in ensemble of atomic or molecular particles is described by the following kinetic equation, which can be derived from the Boltzmann equation:

$$\begin{aligned} \frac{d[A_n]}{dt} = & \sum_{j=1}^{n-1} k_{ex}^{(e)}(A, j; E_e | A, n) [A_j] [e] + \\ & + \sum_{m=n+1}^{m_{\max}} k_{de}^{(e)}(A, m; E_e | A, n) [A_m] [e] - \sum_{j=1}^{n-1} k_{de}^{(e)}(A, n; E_e | A, j) [A_n] [e] - \\ & - \sum_{m=n+1}^{m_{\max}} k_{ex}^{(e)}(A, n; E_n | A, m) [A_n] [e] - k_i^{(e)} [A_n] [e] + k_r^{(e)} [A^+(1)] [e]^2 + \\ & + \sum_{m=n+1}^{m_{\max}} \tilde{A}_{m,n} (A, m | A, n; h\nu) [A_m] + \sum_{j=1}^{n-1} \tilde{B}_{j,n} U_v (1 - \chi_{n,j}) - \\ & - \sum_{j=1}^{n-1} \tilde{A}_{n,j} (A, n | A, j; h\nu) [A_n] - \sum_{m=n+1}^{m_{\max}} \tilde{B}_{n,m} U_v (1 - \chi_{n,m}) + \\ & + \beta_{r,n} [A^+(1)] [e] - \sigma_{i,n} [A_n] U_v (1 - \chi_{i,n}) - k_i^{(M)} (A, n; M | A^+, 1; e; M) [A_n] [M] + \\ & + k_r^{(M)} (A^+, 1; e; M | A, n; M) [A^+(1)] [M] [e] + \sum_{j=1}^{n-1} k_{ex}^{(M)} (A, j; M | A, n; M) [A_j] [M] + \\ & + \sum_{m=n+1}^{m_{\max}} k_{de}^{(M)} (A, m; M | A, n; M) [A_m] [M] - \sum_{j=1}^{n-1} k_{de}^{(M)} (A, n; M | A, j; M) [A_n] [M] - \\ & - \sum_{m=n+1}^{m_{\max}} k_{ex}^{(M)} (A, n; M | A, m; M) [A_n] [M]. \end{aligned} \quad (47)$$

The following definitions were used at formulation of the equation:

$k_i^{(e)}, k_r^{(e)}$  are the rate constants for ionization and recombination at collisions with electron (e);

$k_i^{(M)}, k_r^{(M)}$  are the rate constants for ionization and recombination at collisions with heavy particles (M);

$k_{ex}^{(e)}, k_{de}^{(e)}, k_{ex}^{(M)}, k_{de}^{(M)}$  are the rate constants for excitation (ex) and deactivation (de) at collisions with electrons (e) and heavy particles (M);

$\sigma_{i,n}, \beta_{r,n}$  are the coefficients of photoionization and photorecombination at the level  $n$ ;

$\tilde{A}_{n,j}$  is the Einstein coefficient of spontaneous emission at quantum jump from level  $n$  to level  $j$  ( $j < n$ );

$\tilde{B}_{j,n}$  is the Einstein coefficient of absorption at quantum jump from level  $j$  to level  $n$  ( $j < n$ );



$U_v$  is the volume density of spectral radiative energy;

$[A_n]$  is the concentration of particles A in quantum state  $n$ ;

$[A^+(1)]$  is the concentration of ions at ground state (if  $A_n$  is the ion of a multiplicity of  $z$ , then  $A^+(1)$  is the ion of a multiplicity of  $(z+1)$ ; it is assumed that the ion of the next multiplicity is formed in ground state).

List of arguments for each rate constant contains information about corresponding quantum jump. For example,  $k_{ex}^{(e)}(A, j; E_e | A, n)$  means that the quantum jump to state  $n$  of particle A is conditioned by the initial state  $j$  of particle A, which interacts with electron of energy  $E_e$ . Such a designation is used in quantum mechanics for designation of matrix elements of quantum jumps.

It should be particularly emphasized that Equation (17) is formulated for the only one quantum state. Generally, to predict thermodynamic state of an ensemble of particles in plasma, such an equation should be formulated for each quantum state and for each kind of particles. There are examples of such formulations [19]. But it is obvious that to solve wide class of problems of applied aerophysics there is no need to solve full system of these equations. Therefore, as a rule, the hybrid kinetic models are used. Such hybrid models include both the Boltzmann description of overwhelming majority of quantum states, and radiative-collision kinetic formulations for individual states. To illustrate the hybrid model, which was earlier discussed in many books and papers [1, 20–27], the problem of spectral emissivity behind shock wave will be considered later in the lecture. To create such a hybrid model there is a need to define the individual quantum states for each kind of particle. Example of such an analysis was recently demonstrated by C. Park and W. Huo [28–30]. If the goal function of the problem under consideration is the description of spectral emissivity of molecular gases, then the analysis of the most probable electronic-vibrational bands of emissivity of plasma species behind shock wave is the first step.

#### 4.0 ELECTRONIC KINETICS OF DIATOMIC MOLECULES

Table 4.1 contains the list of electronic vibrational bands of diatomic molecules  $C_2$ ,  $C_2^-$ ,  $C_2^+$ , CN, CO,  $CO^+$ , NO,  $N_2$ ,  $N_2^+$ ,  $NO^+$ ,  $O_2^+$ ,  $O_2$ , which are of practical interest for aerospace applications.

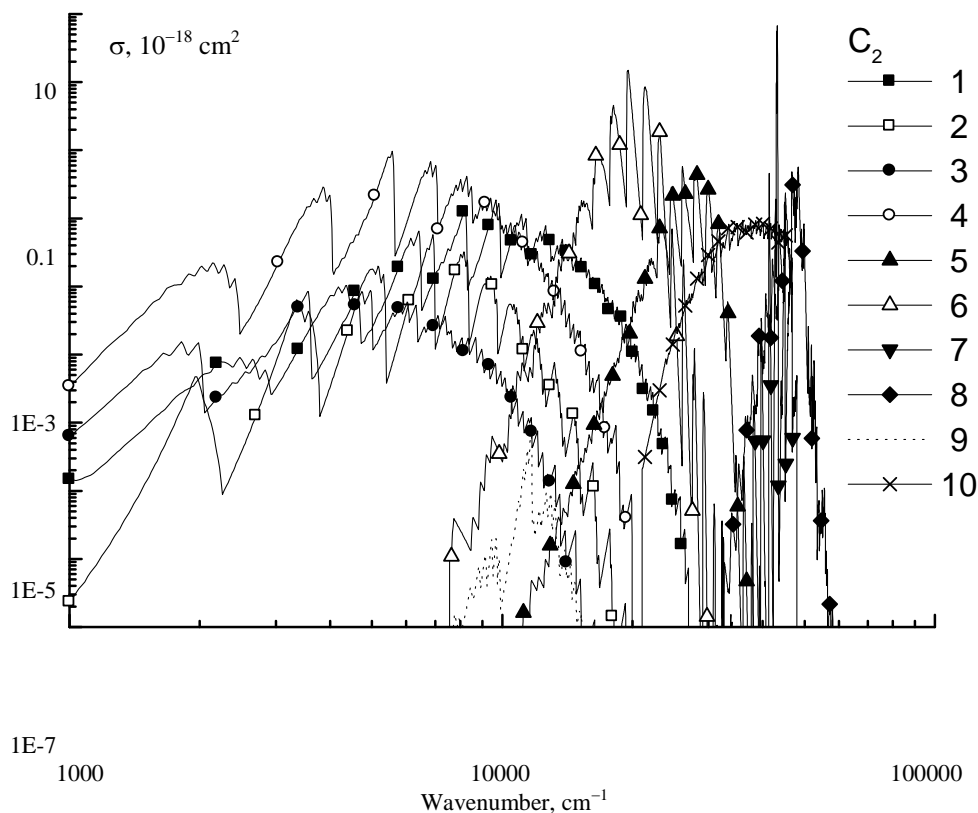
**Table 4.1: Electronic bands of diatomic molecules**

The sequence number	Molecule, electronic transition, name of the transition	Spectral region, $\text{cm}^{-1}$	The range of vibrational states	
			$v' \equiv v_u$	$v'' \equiv v_l$
Molecule $\text{C}_2$				
1	$\text{C}_2, \text{A}^1\Pi_u - \text{X}^1\Sigma_g^+$ , Phillips system	100 ÷ 27000	15	15
2	$\text{C}_2, \text{B}'^1\Sigma_g^+ - \text{A}^1\Pi_u$	100 ÷ 22000	10	10
3	$\text{C}_2, \text{B}^1\Delta_g - \text{A}^1\Pi_u$	100 ÷ 17000	10	15
4	$\text{C}_2, \text{b}^3\Sigma_g^- - \text{a}^3\Pi_u$ , Ballik – Ramsay system	100 ÷ 20000	12	12
5	$\text{C}_2, \text{C}^1\Pi_g - \text{A}^1\Pi_u$ , The Deslandres – D'Azambuja band	8000 ÷ 42000	10	15
6	$\text{C}_2, \text{d}^3\Pi_g - \text{a}^3\Pi_u$ , Swan system	3500 ÷ 35000	12	15
7	$\text{C}_2, \text{D}^1\Sigma_u^+ - \text{X}^1\Sigma_g^+$ , Mulliken system	38000 ÷ 48000	15	15
8	$\text{C}_2, \text{E}^1\Sigma_g^+ - \text{A}^1\Pi_u$	28000 ÷ 60000	10	15
9	$\text{C}_2, \text{E}^1\Sigma_g^+ - \text{D}^1\Sigma_u^+$	100 ÷ 23000	10	10

10	$C_2, e^3\Pi_g - a^3\Pi_u$ , Fox – Herzberg system	21000 ÷ 48500	10	12
Molecule $C_2^-$				
1	$C_2^-, A^2\Pi_u - X^2\Sigma_g^+$	100 ÷ 15000	10	10
2	$C_2^-, B^2\Sigma_u^+ - X^2\Sigma_g^+$	10000 ÷ 30000	10	10
Molecule $C_2^+$				
1	$C_2^+, B^4\Sigma_u^- - A^4\Pi_g$	1000 ÷ 23000	10	12
2	$C_2^+, B^4\Sigma_u^- - X^4\Sigma_g^-$	10000 ÷ 30000	10	10
Molecule CN				
1	CN, $A^2\Pi - X^2\Sigma^+$ , Red system	1000 ÷ 24000	15	15
2	CN, $B^2\Sigma^+ - A^2\Pi$	1000 ÷ 45000	15	15
3	CN, $B^2\Sigma^+ - X^2\Sigma^+$ , Violet system	17000 ÷ 37000	15	15
4	CN, $X^2\Sigma^+ - X^2\Sigma^+$	1000 ÷ 10000	25	25
Molecule CO				
1	CO, $a^3\Sigma^+ - a^3\Pi$ , The Asund bands	100 ÷ 20000	12	12
2	CO, $A^1\Pi - X^1\Sigma^+$ , Fourth Positive system	30000 ÷ 85000	20	29
3	CO, $B^1\Sigma^+ - A^1\Pi$ , The Angstrom system	5000 ÷ 52000	15	20
4	CO, $B^1\Sigma^+ - X^1\Sigma^+$ , The Hopfield – Birge system	74000 ÷ 100000	15	25
5	CO, $b^3\Sigma^+ - a^3\Pi$ , The third positive bands	16000 ÷ 51000	10	21
6	CO, $d^3\Delta - a^3\Pi$ , The triplet bands	100 ÷ 28 000	15	12
7	CO, $e^3\Sigma^- - a^3\Pi$ , The Herman system	100 ÷ 30000	15	12
8	CO, $X^1\Sigma^+ - X^1\Sigma^+$	100 ÷ 8000	25	25
Molecule $CO^+$				
1	$CO^+, A^2\Pi - X^2\Sigma^+$ , Comet-tail systemя	100 ÷ 50000	20	20
2	$CO^+, B^2\Sigma^+ - A^2\Pi$ , Baldet – Johnson system	5000 ÷ 46000	15	20
3	$CO^+, B^2\Sigma^+ - X^2\Sigma^+$ , First negative system	11000 ÷ 60000	15	20
4	$CO^+, X^2\Sigma^+ - X^2\Sigma^+$	10 ÷ 10000	15	15
Molecule NO				
1	NO, $A^2\Sigma^+ - X^2\Pi$ , $\gamma$ - system	16000 ÷ 62000	8	22
2	NO, $B'^2\Delta - X^2\Pi$ , $\beta'$ - system	35000 ÷ 68000	7	22
3	NO, $B^2\Pi - X^2\Pi$ , $\beta$ - system	16000 ÷ 60000	15	22
4	NO, $C^2\Pi - A^2\Sigma^+$	1000 ÷ 20000	4	8
5	NO, $C^2\Pi - X^2\Pi$ , $\delta$ - system	20000 ÷ 65000	4	22
6	NO, $D^2\Sigma^+ - A^2\Sigma^+$	3500 ÷ 15000	4	8
7	NO, $D^2\Sigma^+ - X^2\Pi$ , $\varepsilon$ - system	20000 ÷ 65000	4	22
8	NO, $X^2\Pi - X^2\Pi$	100 ÷ 15000	25	25
Molecule $N_2$				
1, 2	$N_2, a^1\Pi_g - a'^1\Sigma_u^-$	100 ÷ 20000	21	21
3	$N_2, A^3\Sigma_u^+ - X^1\Sigma_g^+$ , Vegard – Kaplan bands	1000 ÷ 75000	21	21
4	$N_2, b'^1\Sigma_u^+ - X^1\Sigma_g^+$ , The Birge – Hopfield 2	54000 ÷ 120000	25	25
5, 6	$N_2, B'^3\Sigma_u^- - B^3\Pi_g$ , «Y» – bands	100 ÷ 20000	21	21
7	$N_2, B^3\Pi_g - A^3\Sigma_u^+$ , First positive system	1000 ÷ 25000	21	21
8	$N_2, b^1\Pi_u - X^1\Sigma_g^+$ , The Birge – Hopfield 1	74000 ÷ 105000	1	12
9, 10	$N_2, W^3\Delta_u - B^3\Pi_g$	10 ÷ 20000	21	21

11	$N_2, D^3\Sigma_u^+ - B^3\Pi_g$ , Forth positive system	28500 ÷ 50000	0	10
12	$N_2, E^3\Sigma_g^+ - A^3\Sigma_u^+$ , The Herman – Kaplan system	30000 ÷ 50000	1	10
13	$N_2, E^3\Sigma_g^+ - B^3\Pi_g$	15000 ÷ 40000	1	15
14	$N_2, E^3\Sigma_g^+ - C^3\Pi_u$	500 ÷ 10000	1	4
15	$N_2, C^3\Pi_u - B^3\Pi_g$ , Second positive system	10000 ÷ 40000	4	19
Molecule $N_2^+$				
1	$N_2^+, A^2\Pi_u - X^2\Sigma_g^+$ , Meinel's auroral system	1000 ÷ 38000	20	20
2	$N_2^+, B^2\Sigma_u^+ - X^2\Sigma_g^+$ , First negative system	7000 ÷ 40000	10	20
3	$N_2^+, C^2\Sigma_u^+ - X^2\Sigma_g^+$ , Second negative system	27000 ÷ 95000	15	20
Molecule $NO^+$				
1	$NO^+, A^1\Pi - X^1\Sigma^+$	39000 ÷ 90000	15	22
Molecule $O_2^+$				
1	$O_2^+, A^2\Pi_u - X^2\Pi_g$ , Second negative system	8000 ÷ 52700	21	21
2	$O_2^+, b^4\Sigma_g^- - a^4\Pi_u$ , First negative system	1000 ÷ 30500	15	20
Molecule $O_2$				
1	$O_2, B^3\Sigma_u^- - X^3\Sigma_g^-$ , Schumann – Runge system	22000 ÷ 57000	14	21

Spectral cross sections of electronic bands presented in Table 4.1 are shown in Figures 4.1–4.10 at temperature  $T = 5000$  K. The number of curve on the each Figure corresponds to the number of the electronic band in Table 4.1. These data were calculated with the use of computer code ASTEROID [31].



**Figure 4.1: Spectral cross section of molecule  $C_2$  at  $T = 5000$  K**

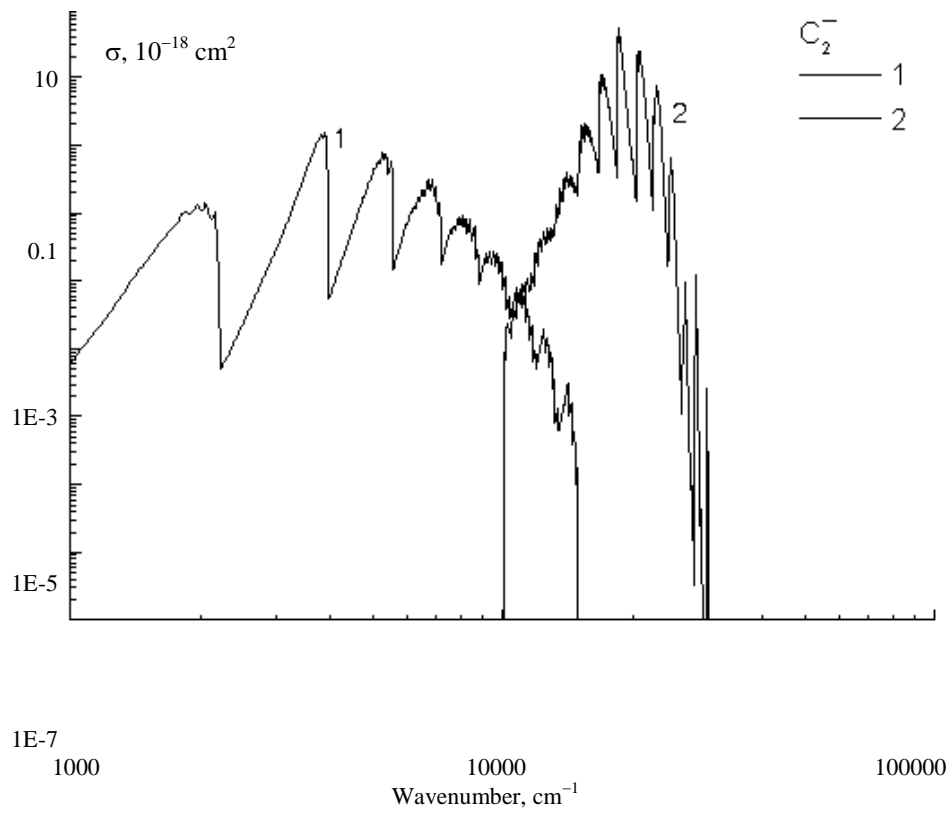


Figure 4.2: Spectral cross section of molecule  $\text{C}_2^-$  at  $T = 5000 \text{ K}$

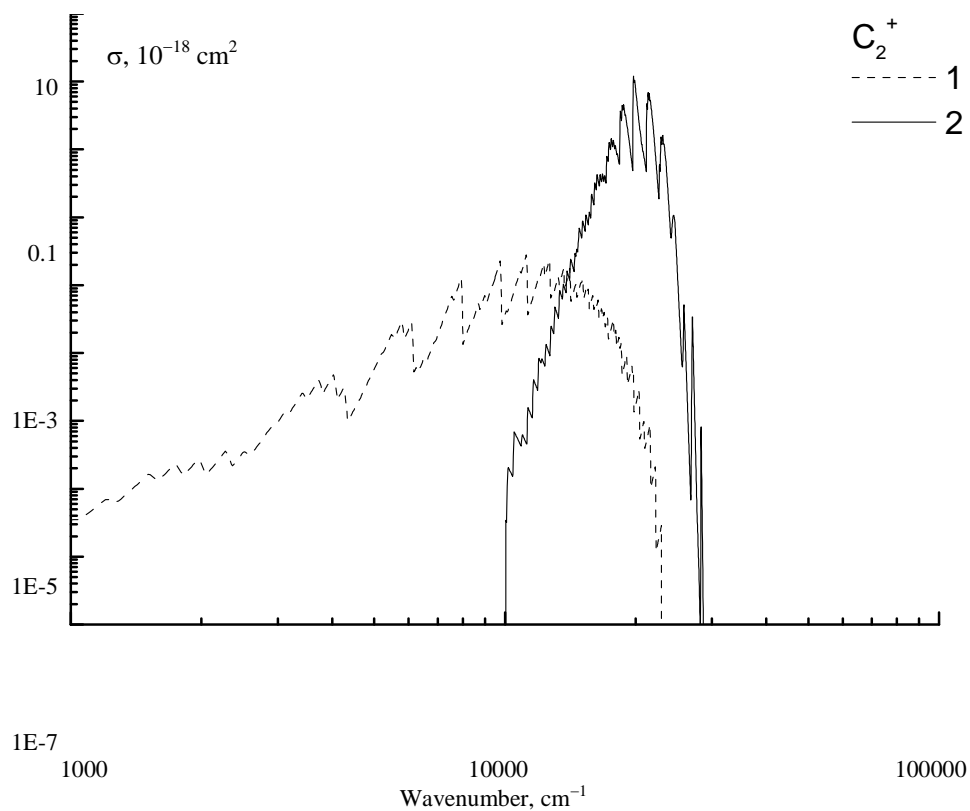


Figure 4.3: Spectral cross section of molecule  $C_2^+$  at  $T = 5000$  K

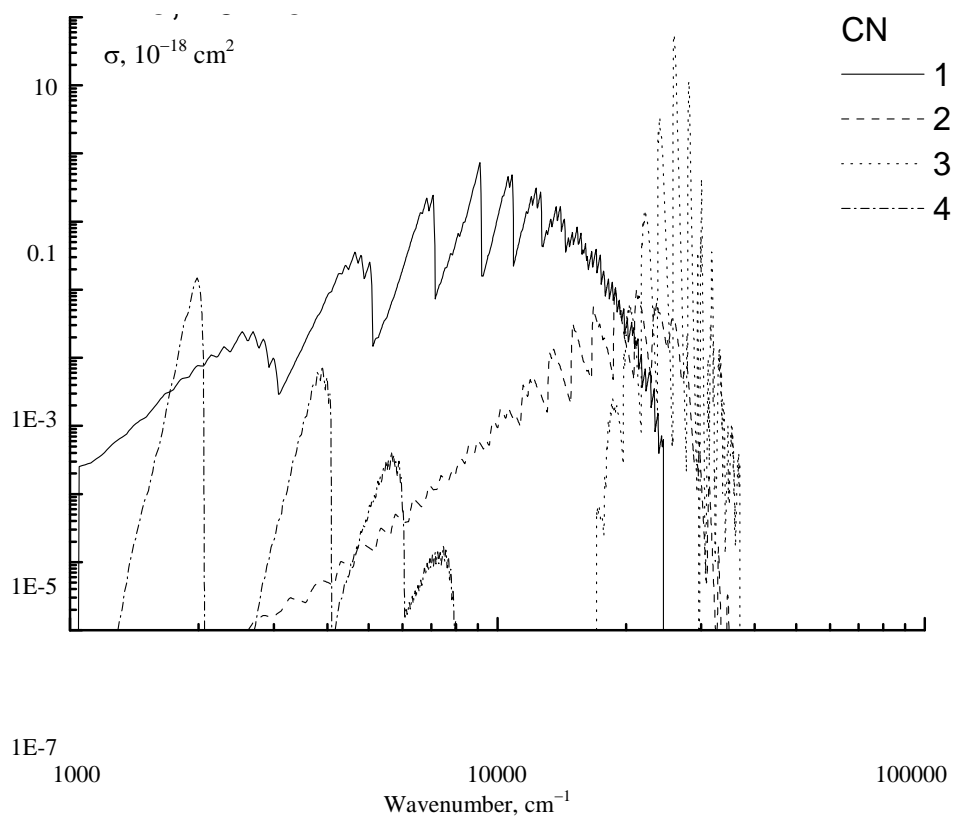


Figure 4.4: Spectral cross section of molecule  $CN$  at  $T = 5000$  K

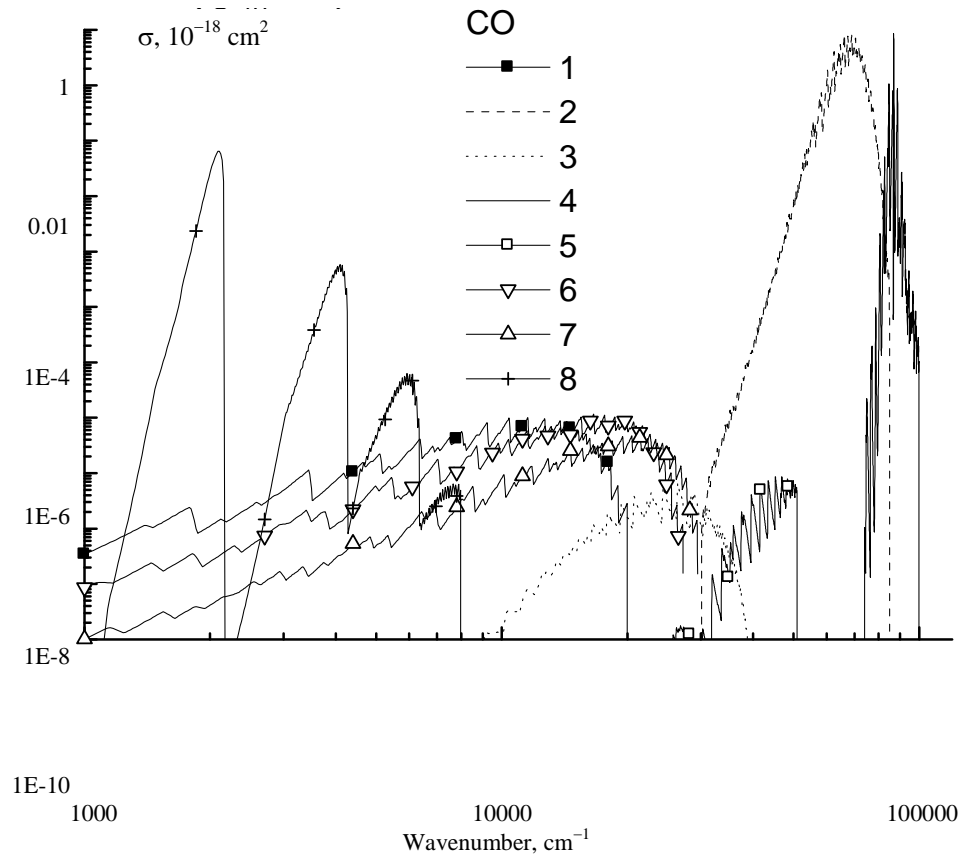


Figure 4.5: Spectral cross section of molecule CO at  $T = 5000 \text{ K}$

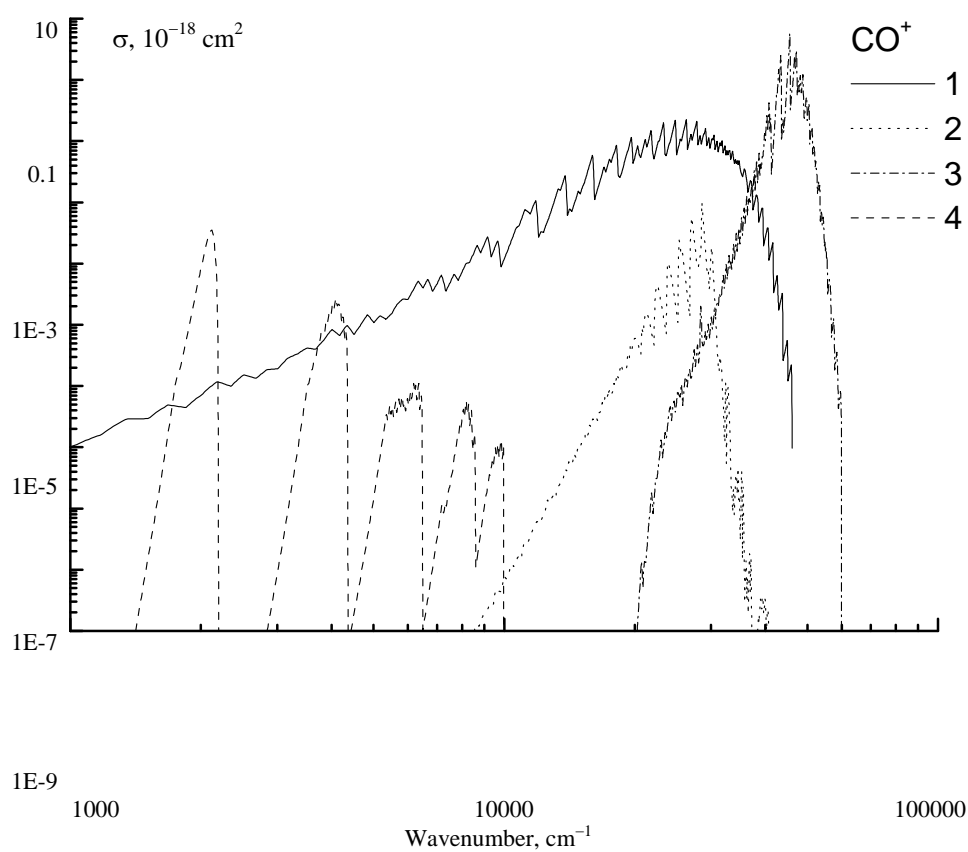


Figure 4.6: Spectral cross section of molecule  $\text{CO}^+$  at  $T = 5000 \text{ K}$

$\sigma, 10^{-18} \text{ cm}^2$

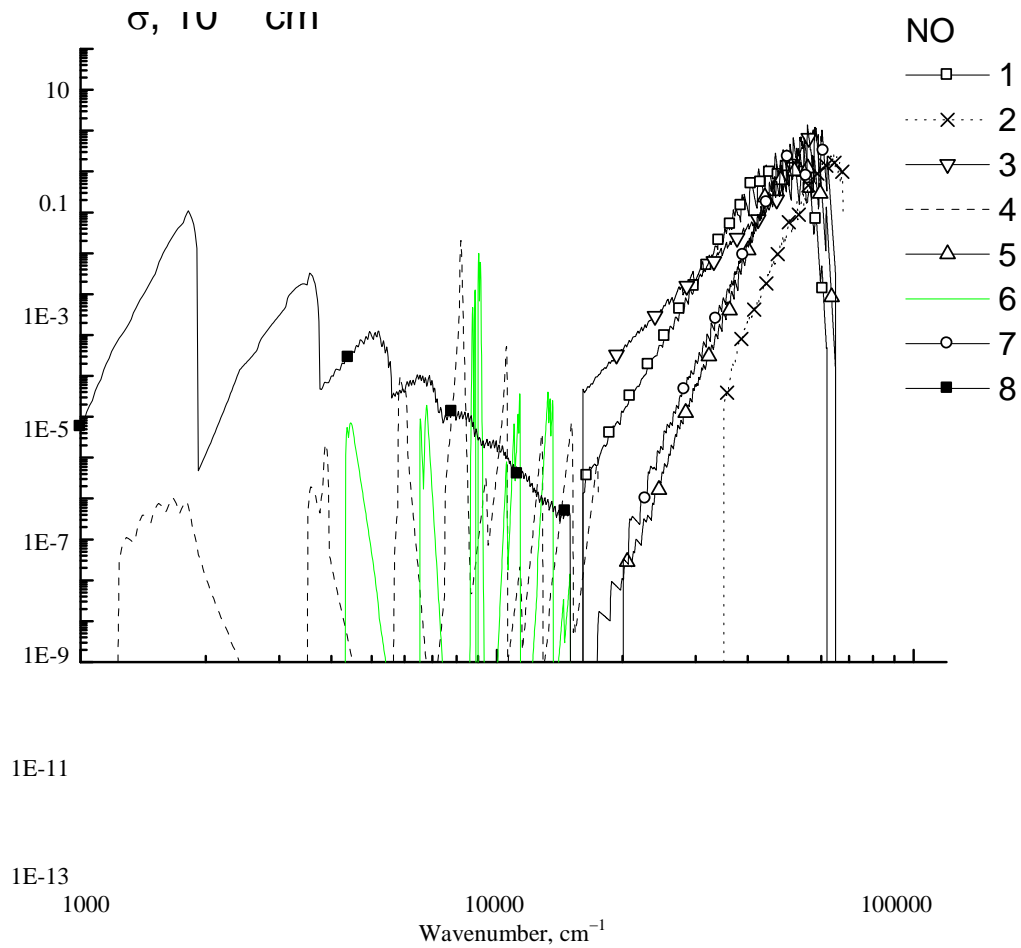


Figure 4.7: Spectral cross section of molecule NO at  $T = 5000 \text{ K}$

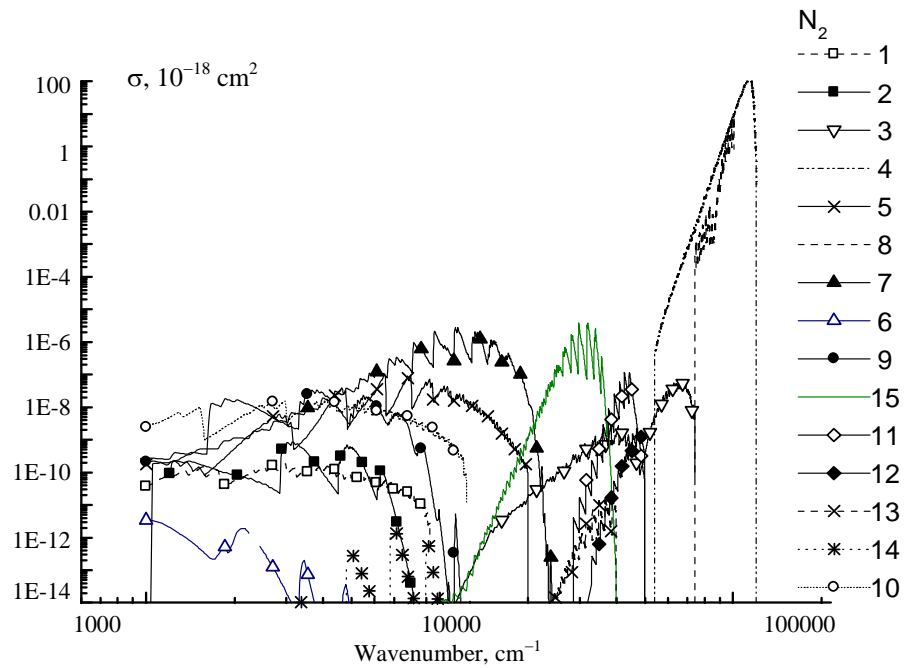


Figure 4.8: Spectral cross section of molecule  $\text{N}_2$  at  $T = 5000 \text{ K}$



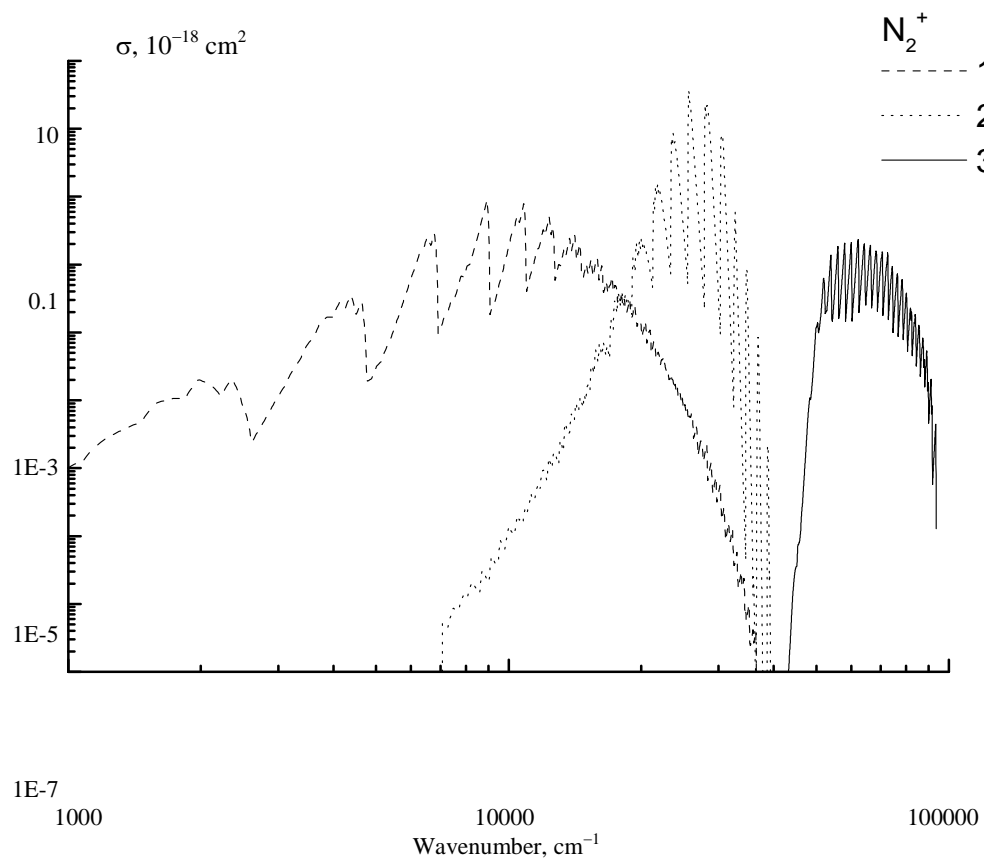


Figure 4.9: Spectral cross section of molecule  $\text{N}_2^+$  at  $T = 5000 \text{ K}$

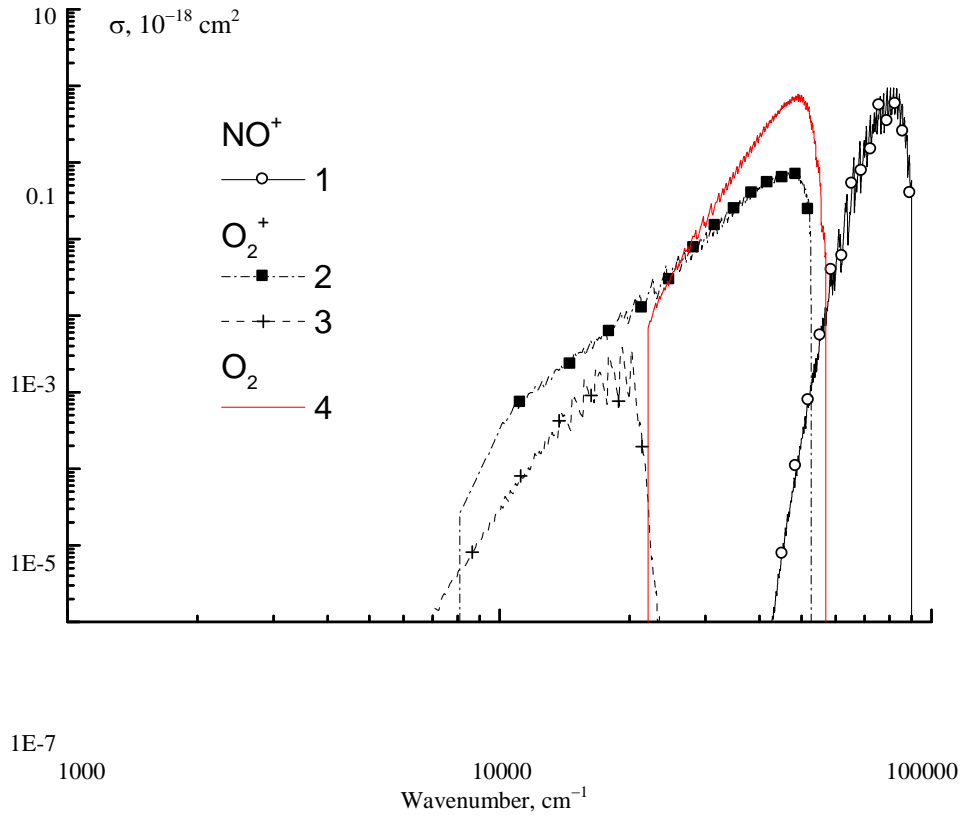


Figure 4.10: Spectral cross section of molecules  $\text{NO}^+$ ,  $\text{O}_2$ ,  $\text{O}_2^+$  at  $T = 5000 \text{ K}$

Comparative analysis of rate constants of excitation and deactivation of electronic states of diatomic molecules show that one of the most significant kinetic processes is the excitation of electronic states at collisions of the molecules with electrons. The theory of this process is considered below.

#### 4.1 Cross sections of excitation of electronic states of diatomic molecules by electronic collisions

Cross section of excitation of electronic level  $\vec{u} = \{u, v_u\}$  at collision of the molecule at electronic level  $l = \{l, v_l\}$  by the electronic collision is

$$\sigma(l, v_l; E_e | u, v_u) = \left| M_e \left( \Delta E_{v_u, v_l}^{u, l} \right) \right|^2 \varphi \left( \frac{E_e}{\Delta E_{v_u, v_l}^{u, l}} \right) q_{v_u, v_l}^{u, l}, \quad (1)$$

where  $E_e$  is the energy of electrons;

$\Delta E_{v_u, v_l}^{u, l}$  is the energy of electronic-vibrational jump;

$\left| M_e \left( \Delta E_{v_u, v_l}^{u, l} \right) \right|^2$  is the square of the matrix element of the electronic-vibrational transition (the function specifies maximal value of the cross section);

$\varphi\left(\frac{E_e}{\Delta E_{v_u, v_l}^{u, l}}\right)$  is the profile of the dependence of the cross section upon on electronic energy;

$q_{v_u, v_l}^{u, l}$  is the Franck – Condon factor of electronic-vibrational transition;

$u, l$  are the quantum numbers of the upper and low states;

$v$  is the vibrational quantum number.

Formula (1) was obtained with the Born – Oppenheimer approximation and the  $r$ -centroid approach [32, 33]. The Bethe – Born approach [34, 35] gives the following value of the matrix element square for excitation of stable states<sup>1</sup>

$$\left| M_e \left( \Delta E_{v_u, v_l}^{u, l} \right) \right|^2 = 1.48 \pi a_0^2 f_{l, u}^{(e)} \left( \frac{Ry}{\Delta E_{v_u, v_l}^{u, l}} \right)^2; \quad (2)$$

and for excitation of unstable levels

$$\left| M_e \left( \Delta E_{v_u, v_l}^{u, l} \right) \right|^2 = 1.48 \pi a_0^2 \frac{d f_{l, u}^{(e)}(\Delta E)}{d(\Delta E)} \left( \frac{Ry}{\Delta E_{v_u, v_l}^{u, l}} \right)^2, \quad (3)$$

where  $Ry$  is the energy of ionization of hydrogen;  $a_0$  is the Bohr radius;  $f_{l, u}^{(e)}$  is the oscillator strength for absorption ( $l \rightarrow u$ );  $\frac{d f_{l, u}^{(e)}(\Delta E)}{d(\Delta E)}$  is the differential oscillator strength related to energy region  $\Delta E$ .

Dependence of the cross section upon on electronic energy and the quantum jump energy has the following form in the Bethe – Born approach:

$$\varphi\left(\frac{E_e}{\Delta E}\right) = 2.7 \left( \frac{\Delta E}{E} \right) \ln \left( \frac{E_e}{\Delta E} \right). \quad (4)$$

Analysis of various experimental data shows that Equation (1) together with (4) describe allowed electronic transitions for any values  $l$  and  $u$ . Substantially more complicated cases are the optically forbidden transitions. These transitions strongly coupled with exchange interaction, and therefore function  $\varphi$  differs for different kinds of electronic transitions.

The oscillator strength  $f_{l, u}^{(e)}$  in Equations (2), (3) can be predicted from ab-initio calculations or experimental data. For these purposes the Refs. [36–38] are recommended.

The Einstein coefficients also can be used for these purposes. It is known that the square of matrix elements of electronic-vibration transition is calculated as follows:

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<sup>1</sup> It is agreed that the stable state has a local minimum of energy. Otherwise, the state is unstable.

$$\left(R_e^{v_u v_l}\right)^2 = \left( \int_0^\infty \Psi_{v_u}(r) R_e(r) \Psi_{v_l}(r) dr \right)^2, \quad (5)$$

where  $\Psi_{v_u}$  и  $\Psi_{v_l}$  are the vibrational wave functions;  $R_e(r)$  is the moment of electronic transition (averaged electronic dipole moment);  $r$  is the inter-nuclear distance.

The Einstein coefficient  $A_{v_l v_u}^{(e)}$  and the oscillator strength in absorption  $f_{v_l v_u}^{(e)}$  are connected to the square of matrix element as follows [37–39]:

$$A_{v_u v_l}^{(e)} = \frac{64\pi^4 \nu^3 (2 - \delta_{0, \Lambda_u + \Lambda_l})}{3hc^3 (2 - \delta_{0, \Lambda_u})} \left(R_e^{v_u v_l}\right)^2 = 2.026 \times 10^{-6} \omega_{v_u v_l}^3 \frac{2 - \delta_{0, \Lambda_u + \Lambda_l}}{2 - \delta_{0, \Lambda_u}} \left(R_e^{v_u v_l}\right)^2, \quad (6)$$

$$f_{v_l v_u}^{(e)} = \frac{8\pi^2 m_e \nu (2 - \delta_{0, \Lambda_u + \Lambda_l})}{3he^2 (2 - \delta_{0, \Lambda_l})} \left(R_e^{v_u v_l}\right)^2 = 3.0376 \times 10^{-6} \omega_{v_u v_l} \frac{2 - \delta_{0, \Lambda_u + \Lambda_l}}{2 - \delta_{0, \Lambda_u}} \left(R_e^{v_u v_l}\right)^2, \quad (7)$$

where  $R_e^{v_u v_l}$  is the moment of electronic-vibrational transition (in atomic units,  $ea_0$ );  $\omega_{v_u v_l}$  is the wavenumber of the transition ( $\text{cm}^{-1}$ ).

For the degenerated quantum levels

$$\sum \left(R_e^{v_u v_l}\right)^2 = (2 - \delta_{0, \Lambda_u + \Lambda_l}) (2S + 1) \left(R_e^{v_u v_l}\right)^2, \quad (8)$$

where  $S$  is the spin multiplicity;  $\Lambda$  is the quantum number of projection of angular momentum on the molecule axis ( $\Lambda = 0, 1, 2, \dots$  for  $\Sigma, \Pi, \Delta, \dots$  states).

The detailed balance condition allows find relation between the oscillator strengths at emission and absorption:

$$f_{u, l} = \frac{2 - \delta_{0, \Lambda_l}}{2 - \delta_{0, \Lambda_u}} f_{l, u}. \quad (9)$$

Then the oscillator strength in emission is connected with the Einstein coefficient as following:

$$f_{v_u, v_l} = 1.5 \frac{A_{v_u, v_l}}{\omega_{v_u, v_l}^2} \frac{2 - \delta_{0, \Lambda_u}}{2 - \delta_{0, \Lambda_l}}.$$

Now one can obtain formula for cross section of electronic excitation for dipole transitions:

$$\sigma(l, v_l; E_e | u, v_u) = 1.5 \pi a_0^2 \frac{A_{v_u, v_l}}{\omega_{v_u, v_l}^2} \left( \frac{R_y^\omega}{\omega_{v_u, v_l}} \right)^2 \varphi^*, \quad (10)$$

where

$$\varphi^* = 2.7 \frac{\omega_{v_u, v_l}}{8067 E_{e, [\text{eV}]}} \ln \left( \frac{8067 E_{e, [\text{eV}]}}{\omega_{v_u, v_l}} \right).$$

Cross section of excitation of the given electronic-vibrational state  $\vec{u} = \{u, v_u\}$  is calculated by summation over all vibrational states of the lower electronic state:

$$\sigma(l; E_e | u, v_u) = \sum_{v_l} \sigma(l, v_l; E_e | u, v_u) \frac{Q_R(l, v_l)}{Q_{VR}(l)} e^{-1.44(E_{v_l}/kT_v)},$$

where

$$Q_R(l, v_l) = \sum_{J=J_{\min}}^{J_{\max}(v_l)} (2J+1) e^{-\frac{E_J - E_{J, \min}}{kT_J}},$$

$$Q_{VR}(l) = \sum_{v=0}^{v_{\max}(l)} \sum_{J=J_{\min}}^{J_{\max}(v_l)} (2J+1) e^{-\frac{E_v - E_{v=0}}{kT_v}} e^{-\frac{E_J - E_{J, \min}}{kT_J}}.$$

And, finally, it is possible to calculate total cross section of excitation of upper electronic state at collision of molecules in lower electronic states with electrons:

$$\sigma(l; E_e | u) = \sum_{v_l} Q_R(l, v_l) \frac{e^{-1.44(E_{v_l}/kT_v)}}{Q_{VR}(l)} \sum_{v_u} \sigma(l, v_l; E_e | u, v_u) Q_R(u, v_l) \frac{e^{-1.44(E_{v_u}/kT_v)}}{Q_{VR}(u)}. \quad (11)$$

Once a given cross section has been calculated, the rate constants for quantum transition  $l, v_l \rightarrow u, v_u$  can be determined.

If  $f(E_e)$  is the energy distribution functions of electrons, then

$$k_{ex}(l, v_l; f(E_e) | u, v_u) = \left| M_{e, v_u, v_l}^{u, l} \right|^2 q_{v_u, v_l}^{u, l} \frac{\int \Phi \left( \frac{E_e}{\Delta E_{v_u, v_l}^{u, l}} \right) E_e f(E_e) dE_e}{\int \sqrt{E_e} f(E_e) dE_e}. \quad (12)$$

To calculate the rate constant for excitation of the *electronic-vibrational* level from electronic state  $l$ , there is a need in averaging of (9) over all vibrational states  $v_l$ :

$$k_{ex}(l; f(E_e) | u, v_u) = \sum_{v_l} x(l, v_l) k_{ex}(l, v_l; f(E_e) | u, v_u) = \sum_{v_l} x(l, v_l) \left| M_{e, v_u, v_l}^{u, l} \right|^2 q_{v_u, v_l}^{u, l} J_{v_u, v_l}^{u, l}, \quad (13)$$

where

$$J_{v_u, v_l}^{u, l} = \frac{\int \Phi \left( \frac{E_e}{\Delta E_{v_u, v_l}^{u, l}} \right) E_e f(E_e) dE_e}{\int \sqrt{E_e} f(E_e) dE_e}.$$

The rate constant for excitation of electronic state  $u$  is

$$k_{ex}(l; f(E_e)|u) = \sum_{v_u} k_{ex}(i; f(E_e)|u, v_u). \quad (14)$$

For the Maxwell – Boltzmann distribution functions the rate constants were obtained in Refs. [40, 41].

For the case of the Maxwellian distribution function of electrons, one can derive

$$k_{ex}(l; E_e|u) = 6.69 \times 10^{-9} \frac{1}{T^{3/2}} \int_0^\infty \sigma(l; E|u) E e^{-(E/kT)} dE, \frac{\text{cm}^3}{\text{s}}. \quad (15)$$

Results of calculations of averaged cross sections of electronic excitation of allowed quantum transitions are presented in Figure 4.11. These calculations were performed by the author with the use of Eq. (15).

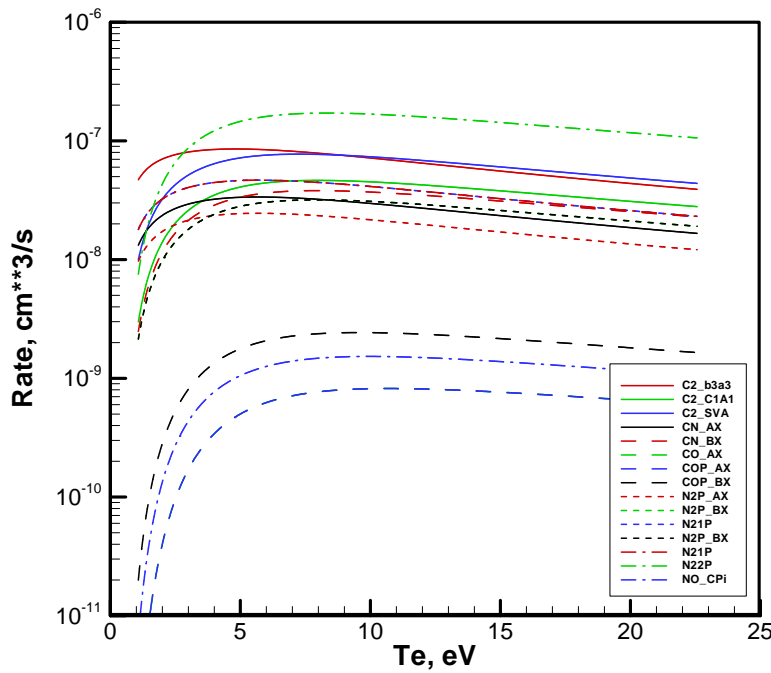


Figure 4.11: Averaged cross sections of electronic excitation of allowed quantum transitions

To calculate cross sections of electronic excitation of forbidden quantum transitions consideration must be given to the exchange interaction. Cross sections of the forbidden transitions achieves its maximum closer to the energetic threshold of the quantum transition, usually at  $E_e^{\max}/\Delta E = 1.25 \div 1.6$ . Maximum values of such a cross section close to those for optical allowed transitions. More detailed information one can find in Refs. [28, 42, 43].

#### 4.2. Excitation and deactivation of electronic states at collisions with heavy particles

Averaged over Maxwellian distribution function rate coefficient of excitation of electronic states of atoms (A) or molecules (AB) at collision with heavy particle (B) is obtained in the following form [9, 10]:

$$k_{ex}(AB, M; \vec{l}; T | AB, M; \vec{u}) = 32\pi a_0^2 \left( \frac{Ry}{\Delta E_{l,u}} \right) f_{l,u} \left( \frac{kT}{\pi M} \right)^{1/2} \frac{m_e}{m_{AB}} \left( 1 + \frac{2kT}{\Delta E_{l,u}} \right) e^{-(\Delta E_{l,u}/kT)}. \quad (16)$$

For the deactivation process one can derive with the use of the detailed balance relation

$$k_{de}(AB, M; \vec{u}; T | AB, M; \vec{l}) = 32\pi a_0^2 \left( \frac{Ry}{\Delta E_{l,u}} \right) f_{l,u} \left( \frac{kT}{\pi M} \right)^{1/2} \frac{m_e}{m_{AB}} \left( 1 + \frac{2kT}{\Delta E_{l,u}} \right). \quad (17)$$

Examples of numerical values of rate coefficients of deactivation of excited atoms by molecules at  $T = 300$  K are presented in Table 4.2.

**Table 4.2: Rate coefficients of deactivation of excited atoms A\* by molecules M at  $T = 300$  K [44]**

M	O( <sup>1</sup> D)	O( <sup>1</sup> S)	O( <sup>5</sup> S)	N( <sup>2</sup> D)	N( <sup>2</sup> P)
N <sub>2</sub>	3.0	<10 <sup>-6</sup>	2.4	–	2×10 <sup>-7</sup>
O <sub>2</sub>	4.1	[4.9×10 <sup>-12</sup> e <sup>-860/T</sup> ]	14	0.6	0.46
CO	<5	5×10 <sup>-2</sup> ÷ 5×10 <sup>-3</sup>	4.8	0.6	–
NO	–	8 ÷ 55	11	7	3.4
CO <sub>2</sub>	12	[10 <sup>-11</sup> e <sup>-1385/T</sup> ]	48	5×10 <sup>-3</sup>	6×10 <sup>-2</sup>

**Table 4.3: Rate coefficients of deactivation of excited electronic states of diatomic molecules by the collisions with heavy particles,  $k_{de}$ , 10<sup>-11</sup> cm·s<sup>-1</sup> [44]**

	N <sub>2</sub>	O <sub>2</sub>	CO	NO	CO <sub>2</sub>
N <sub>2</sub> (A <sup>3</sup> Σ <sup>+</sup> )	4.5×10 <sup>-6</sup> ÷ 1.9×10 <sup>-7</sup>	0.36 ÷ 0.65	2.2 ÷ 2.4	8.5	0.2
N <sub>2</sub> (B <sup>3</sup> Π <sub>g</sub> )	0.5 ÷ 7.5	30	–	3.7 ÷ 17	5.5 ÷ 33
N <sub>2</sub> (C <sup>3</sup> Π <sub>u</sub> )	1 ÷ 2	30	–	–	–
CO(a <sup>3</sup> Π)	3.8 ÷ 7.3	11	14	1.8 ÷ 3.2	3.4
NO(B <sup>2</sup> Π)	–	–	–	8 ÷ 10	1.0
NO(A <sup>2</sup> Σ)	–	–	–	12.5	–

Rate coefficients of deactivation as a rule slow decrease with temperature increasing:

$$k \sim \left( \frac{300}{T} \right)^{0.1}.$$

However, there are cases of rate coefficient increases with the temperature increasing.

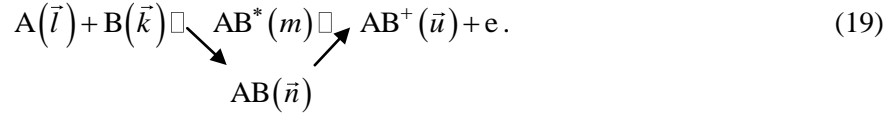
### 4.3 Associative ionization

Rate coefficient of association ionization at collisions of atoms and molecules is estimated as followed:

$$k_f \left( A, B; \vec{l}, \vec{k} \middle| AB^+; \vec{u} \right) \cong \left( 10^{-10} \div 2 \times 10^{-13} \right) e^{-(\Delta E/kT)}, \text{ cm}^3/\text{s}, \quad (18)$$

where  $\Delta E$  is the energetic threshold.

Common scheme of associative ionization is expressed as follows:

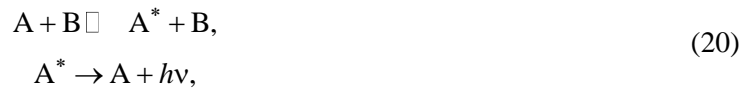


The associative ionization is the two-stage process. There are two scheme of the process. For the first scheme, at the first stage unstable molecule  $AB^*(m)$  is arisen after collisions of two particles (for example, two atoms). Molecular ion  $AB^+(\vec{u})$  is arisen at the second stage due to autoionization process. For the second scheme (see kinetic scheme (19)), at the first stage the stable state of molecule  $AB(\vec{n})$  is arisen. At the second stage a molecular ion  $AB^+(\vec{u})$  is arisen due to autoionization. Inverse kinetic process, the dissociative recombination, runs in accordance with similar kinetic scheme.

Detail analysis of rate coefficients of excitation and deactivation of the electronic states of diatomic molecules one can find in Ref. [29].

#### 4.4 Radiative deactivation of electronic states of diatomic molecules

There are Nonequilibrium conditions in gases and plasma when the filling of upper levels due to collisions becomes less then rate of the level deactivation due to spontaneous emission of radiation. Such a situation can be described by the following kinetic scheme:



where  $A^*$  is the excited state of atom or molecule.

Kinetic equation for the rate of the process is formulated in the following form:

$$\frac{d[A^*]}{dt} = k_f [A][B] - k_r [A^*][B] - \frac{[A^*]}{\tau_{rad}}, \quad (21)$$

where  $\tau_{rad}$  is the radiative life time of the excited state.

From this equation one can derive formula for  $[A^*]$ :

$$[A^*] = \frac{K(T)[A] - \frac{d[A^*]}{dt} \frac{1}{k_r[B]}}{1 + \frac{1}{\tau_{rad}k_r[B]}}, \quad (22)$$



where  $K(T) = k_f / k_r$ .

At large density of gas the collision frequency is high and we have conditions of equilibrium:

$$\frac{d[A^*]}{dt} = 0,$$

and also  $\tau_{rad} k_r [B] \gg 1$ , therefore

$$[A^*] = [A] \cdot K(T). \quad (23)$$

So, in this case the emissivity is proportional to density.

Otherwise, at low density, at steady-state conditions

$$\frac{d[A^*]}{dt} \approx 0,$$

the reverse situation is realized  $\tau_{rad} k_r [B] \ll 1$ , then

$$[A^*] = [A][B] \cdot k_f \tau_{rad}. \quad (24)$$

In this case the emissivity is proportional to density  $\rho^2$ .

Below is given the formulas for calculation  $\tau_{rad}$ .

The life time of excited electronic-vibrational state is given by the following formula [36]:

$$\frac{1}{\tau_{u,v_u;l,v_l}} = \frac{64\pi^4}{3h} g_u S_e(r_{v_u,v_l}) q_{v_u,v_l} \omega_{v_u,v_l}^3, \quad (25)$$

where  $g_u = \frac{1}{(2 - \delta_{0,\Lambda_u})(2S + 1)}$ ;  $S_e$  is the strength of the electronic transition in atomic units;

$$\frac{64\pi^4}{3h} = 2.03 \times 10^{-6}.$$

There is correlation between the oscillator strength in emission and the strength of the electronic transition:

$$f_{u,v_u;l,v_l} = 3.04 \times 10^{-6} g_u S(r_{v_u,v_l}) q_{v_u,v_l} \omega_{v_u,v_l}, \quad (26)$$

therefore

$$\frac{1}{\tau_{u,v_u;l,v_l}} = 0.668 f_{u,v_u;l,v_l} \omega_{v_u,v_l}^2 \quad (27)$$

or, taking into account, that

$$f_{u,v_u;l,v_l} = 1.5 \frac{A_{u,v_u;l,v_l}}{\omega_{v_u,v_l}^2}, \quad (28)$$

one can derive

$$\frac{1}{\tau_{u,v_u;l,v_l}} = A_{u,v_u;l,v_l}. \quad (29)$$

The life time of the upper electronic-vibrational state is defined by the summation over vibrational states of the low electronic level:

$$\frac{1}{\tau_{u,v_u;l}} = \sum_{v_l} A_{u,v_u;l,v_l}.$$

The life time of the upper electronic level is

$$\frac{1}{\tau_{u,l}} = \sum_{v_u} \sum_{v_l} A_{u,v_u;l,v_l}. \quad (30)$$

Tables RD10 contain life times for some electronic and electronic-vibrational states, calculated by the author with the use of ab-initio data [31].

## 5.0 ELECTRONIC KINETICS OF ATOMS AND IONS

Analysis of radiative-collisional processes in Chapter 3 showed that to create computational models of electronic kinetics in atomic plasma there is a need to use or quasiclassical or quantum mechanics models of inelastic collisions of heavy particles (atoms, ions) and electrons.

Both approaches are the particular cases of the quantum theory of atomic, molecular and electronic scattering [Alder; Burke]. The following approximate methods are in wide applications in the theory of quantum collisions:

- the method of strong coupling [45–48];
- the Born approximate method [12, 13];
- the Glauber approximate method [47, 48];
- the classical approximation [49].

Results of the quantum theory of scattering are used in aerophysics usually in the following forms:

- approximation of the quantum mechanics calculations;
- quasiclassical or even classical approximate models;
- approximate quantum mechanics models.

Below examples of the approaches will be considered.

### 5.1 Approximate relations for electronic excitation and ionization

Approximate formulas obtained by Drawin [9, 10] are in common use in different RC-models. For rate constants of electronic excitation of optically allowed transitions ( $l_l \neq l_u$ ;  $l_l, l_u$  are the orbital quantum number of the upper and lower states):

$$k_{ex}(l, u) = \sqrt{\frac{8kT_e}{\pi m_e}} 4\pi a_0^2 \alpha \left( \frac{I_H}{kT_e} \right)^2 I_1(a), \quad (1)$$

where  $\alpha = 0.05$ ;  $I_H$  is the ionization potential of hydrogen;

$$I_1(a) = 0.63a^{-1.65}e^{-a}, \quad (2)$$

$$a = \frac{E_u - E_l}{kT_e}.$$

For the optically forbidden transitions the rate constant is formulated as follows:

$$k_{ex}(l, u) = \sqrt{\frac{8kT_e}{\pi m_e}} 4\pi a_0^2 \alpha \left( \frac{E_u - E_l}{kT_e} \right)^2 I_2(a), \quad (3)$$

where  $I_2(a) = 0.24e^{-a}a^{-1.49}$ .

Examples of the use such relations for analysis shock wave structure are presented in [19].

To calculate rate constants of ionization at electron-atom collisions it is enough to use  $\alpha = 1$  and

$$a = \frac{E_{ioniz} - E_l}{kT_e}. \quad (4)$$

### 5.2 Comments about classical theory of ionization of atoms by electronic impact

The first classical model of collisional electron-atom ionization was created by Thomson [50]. The model was formulated for two colliding electrons, one of them is immovable. Classical electrodynamics [51] allows predict probability for the moving electron to gain energy  $\varepsilon$  in the region  $(\varepsilon \div \varepsilon + d\varepsilon)$ :

$$d\sigma_e = \frac{2\pi}{v_e^2} = \frac{d\Delta\varepsilon}{(\Delta\varepsilon)^2}. \quad (5)$$

Because at the ionization

$$\Delta\varepsilon > I,$$

where  $I$  is the ionization potential of the atom, then for ionization of one electron one can derive

$$\sigma_i^{(1)} = \frac{\pi}{I^2} f\left(\frac{E}{I}\right), \quad (6)$$

where

$$f(x) = \frac{1}{x} - \frac{1}{x^2}. \quad (7)$$

To calculate total cross section there is a need in summation over all states:

$$\sigma_i = \sum_j n_j \frac{\pi}{I_j^2} f\left(\frac{E}{I_j}\right), \quad (8)$$

where  $n_j$  is the number of equivalent electrons.

Note, that the energy distribution function of ionized electrons can be predicted by Equation (5).

The Thomson theory gives correct qualitative dependence of cross section versus velocity of electrons. But the location and magnitude of the cross section maximum is predicted incorrectly. Some later models took into account movement of electron-target [52]. The Bethe quantum mechanics model [53] gave asymptotic interpretation of the Thomson classical model. Nevertheless, the Thomson model represents practical interest until the present, because:

- 1) The model unsure reasonable agreement with experimental data at near-threshold regions;
- 2) The model was modified by Gryzinski and Kingston with success [54] in the frame of classical theory. An approximate function  $f(x)$  was suggested, which allows make better the Thomson classical theory:

$$f(x) = \frac{1}{x} \left( \frac{x-1}{x+1} \right)^{3/2} \left[ 1 + \frac{2}{3} \left( 1 - \frac{1}{2x} \right) \ln(e + \sqrt{x-1}) \right]. \quad (9)$$

### 5.3 Approximations of the quantum mechanical calculations

Systematic calculations of cross sections and rate constants of excitation and ionization were performed in [55]. Cross section and rate constant of excitation of atomic states at collisions with electrons is presented in the form:

$$\sigma(0/1) = \left[ \pi a_0^2 \right] \left( \frac{Ry}{\Delta E} \right)^2 \left( \frac{E_1}{E_0} \right)^{3/2} \frac{Q_{\chi_m}}{2l_0 + 1} \Phi(u), \quad (10)$$

$$\langle \sigma(0/1)v \rangle = 10^{-8} \left( \frac{Ry}{\Delta E} \frac{E_1}{E_0} \right)^{3/2} \frac{Q_{\chi_m}}{2l_0 + 1} e^{-\beta} G(\beta), \frac{\text{cm}^3}{\text{s}}, \quad (11)$$

where  $I_0, I_1$  are the energy of ionization from the ground (0) and excited (1) levels;  $\Delta E = I_1 - I_0$ ;  $Ry = 109737 \text{ cm}^{-1}$ ;  $a_0 = 0.529 \times 10^{-8} \text{ cm}$ ;  $l_0, l_1$  are the orbital moments of electron in the initial (0) and final (1) states.

The energy of incident electron is expressed in threshold units:

$$u = \frac{E'}{\Delta E} = \frac{E}{\Delta E} - 1, \quad \beta = \frac{\Delta E}{kT},$$

where  $E$  is the energy of the incident electron.

Ionization cross section from shell  $l_0^m$  is presented as follows:

$$\sigma_i = \left[ \pi a_0^2 \right] \frac{m}{2l_0 + 1} \left| \frac{Ry}{E_0} \right|^2 \Phi_i(\tilde{u}), \quad (12)$$

$$\langle \sigma_i v \rangle = 10^{-8} \frac{m}{2l_0 + 1} \left| \frac{Ry}{E_0} \right|^{3/2} e^{-\tilde{\beta}} G_i(\tilde{\beta}), \frac{\text{cm}^3}{\text{s}}, \quad (13)$$

where 
$$\tilde{u} = \frac{E_1}{|E_0|}, \quad \tilde{\beta} = \frac{|E_0|}{kT}; \quad (14)$$

$E_1$  is the energy of electrons in continuum.

Photorecombination on the state 0 with energy  $E_0$  is calculated as follows:

$$\sigma_r^{ph} = \left[ \pi a_0^2 \right] \times 10^6 Q_r \Phi_r(u), \quad (15)$$

$$\langle \sigma_r^{ph} v \rangle = 10^{-14} Q_r \left| \frac{E_0}{Ry} \right|^{1/2} G_r(\beta), \frac{\text{cm}^3}{\text{s}}. \quad (16)$$

To calculate total cross section over all states energy  $E_0$  corresponds to the ground state.

For the sake of convenience the following analytical formulas were suggested [55]:

$$\Phi(u) = C \left( \frac{u}{u+1} \right)^{1/2} \frac{1}{u+\varphi}, \quad (17)$$

$$G(\beta) = A \frac{\sqrt{\beta(\beta+1)}}{\beta+x}, \quad (18)$$

$$z=1, \quad \Delta S=1. \quad (19)$$

For the intercombination transitions the same formula looks like follows:

$$G(\beta) = A \frac{\beta^{3/2}}{\sqrt{1+\beta}(\beta+x)}, \quad z=1, \Delta S=1. \quad (20)$$

At  $z \geq 2$  (excitation of ions)

$$\left. \begin{aligned} \Phi(u) &= \frac{\square}{u + \varphi} \\ G(\beta) &= A \frac{(\beta+1)\sqrt{\beta}}{\beta+x} \end{aligned} \right\} z \geq 2, \Delta S = 0, \quad (21)$$

and for intercombination transitions

$$G(\beta) = A \frac{\beta^{3/2}}{\beta+x}, \quad z \geq 1, \Delta S = 1. \quad (22)$$

Table 5.1: Fitting coefficients in formulas (17)–(22)

Element	Transition	C	$\varphi$	A	$\chi$
C	2p – 3s	10.3	8.31	2.56	0.119
	2p – 3p	7.55	1.01	12.7	0.845
N	2p – 3s	10.6	8.40	2.62	0.12
	2p – 3p	6.70	0.99	11.7	0.822
	2p – 4s	–	–	1.71	0.113
	2p – 3d	29.1	9.94	6.09	0.131
O	2p – 3s	9.66	8.60	2.35	0.135
	2p – 3p	5.45	0.97	9.64	0.893
	2p – 4s	5.83	7.24	1.68	0.143
	2p – 3d	23.6	9.92	4.96	0.132

It should be stressed that formulas (10), (11), (15), (16) contain angular coefficients  $Q_{\chi_m}$  and  $Q_r$ .

For transitions between the fine structure components of atomic terms, that is for

$$[S_p L_p] l_0 S L_0 J_0 \rightarrow [S_p L_p] l_1 S L_1 J_1 \quad (23)$$

the factor  $Q_{\kappa}^J$  is

$$Q_{\kappa}^J(SL_0 J_0; SL_1 J_1) = (2L_0 + 1)(2J_1 + 1) \left\{ \begin{matrix} L_0 & J_0 & S \\ J_1 & L_1 & \kappa \end{matrix} \right\} Q_{\kappa}(SL_0; SL_1), \quad (24)$$

where  $Q_{\kappa}(SL_0; SL_1)$  is the angular factor for transition between terms;  $[S_p L_p]$  is the total spin and orbital moment of the parent term.

For transition from any level  $J_0$  of the term  $SL_0$  to all components of fine structure of the term  $SL_1$  the factor  $Q_{\kappa}$  is

$$Q_{\kappa}(SL_0 J_0; SL_1) = \sum_{J_1} Q_{\kappa}^J(SL_0 J_0; SL_1 J_1) = Q_{\kappa}(SL_0; SL_1). \quad (25)$$

Note, that this coefficient does not depend on  $J_0$ .

The angular factor for transition from all components of the fine structure of  $SL_0$  term to separate level  $J_1$  of term  $SL_1$  is presented as follows:

$$Q_{\kappa}^J(SL_0; SL_1 J_1) = \frac{1}{(2S+1)(2L_0+1)} \sum_{J_0} (2J_0+1) Q_{\kappa}^J(SL_0 J_0; SL_1 J_1) = \frac{2J_1+1}{(2S+1)(2L_1+1)} Q_{\kappa}(SL_0; SL_1). \quad (26)$$

The factors  $Q_{\kappa}$  for transition between terms can be calculated by computer code presented in [56].

## 6.0 OSCILLATOR STRENGTH DATA PROCESSING AUTOMATION

The computer-oriented methods of creation of the Radiative-Collision models have come into importance due to the following reasons:

- 1) The enormous volumes of the spectral information;
- 2) The possibilities for systematization of the information.

Family of codes ASTEROID exemplifies such a computer tools [31, 57]. General principles of creation of such codes will be considered on the example of calculations of oscillator strengths for arbitrary light atom particles.

The database [58] of energy levels of atoms and ions is used for the calculation of the atomic lines parameters. Typical computer representation on atomic energy levels for atomic particles N, N<sup>+</sup>, O, O<sup>+</sup>, C, C<sup>+</sup> is shown in Table 6.1. Here the fragment is shown. The full tables are presented in [31, 59].

**Table 6.1: Computer representation of the atomic energy level parameters**

-----												
ATOM = N    Z = 1.    ATOMW = 14.												
NTSMAX = 228    NIMAX = 90    NPterm = 2												
Comments: #S=2S+1,    #S''=2S''+1.												
No.	E(n,l)	J	n	l	q	#S	L	$\pi$	#S''	L''	$\pi''$	sh
-----												
1	0.	1.5	2	1	3	4	0	0	0	0	0	0
2	19223.	2.5	2	1	3	2	2	0	0	0	0	0
2	19231.	1.5	2	1	3	2	2	0	0	0	0	0
3	28840.	1.5	2	1	3	2	1	0	0	0	0	0
3	28840.	0.5	2	1	3	2	1	0	0	0	0	0
4	83285.5	0.5	3	0	1	4	1	1	3	1	1	0
4	83319.3	1.5	3	0	1	4	1	1	3	1	1	0
4	83366.0	2.5	3	0	1	4	1	1	3	1	1	0
5	86131.4	0.5	3	0	1	2	1	1	3	1	1	0
5	86223.2	1.5	3	0	1	2	1	1	3	1	1	0
6	88109.5	2.5	2	1	4	4	1	1	0	0	0	0
6	88153.4	1.5	2	1	4	4	1	1	0	0	0	0
6	88173.0	0.5	2	1	4	4	1	1	0	0	0	0
7	93582.3	0.5	3	1	1	3	1	0	3	1	1	0
8	94772.2	0.5	3	1	1	4	2	0	3	1	1	0
8	94794.8	1.5	3	1	1	4	2	0	3	1	1	0
8	94832.1	2.5	3	1	1	4	2	0	3	1	1	0
8	94883.1	3.5	3	1	1	4	2	0	3	1	1	0

9	95476.5	0.5	3	1	1	4	1	0	3	1	1	0
9	95494.9	1.5	3	1	1	4	1	0	3	1	1	0
9	95533.2	2.5	3	1	1	4	1	0	3	1	1	0
10	96751.7	1.5	3	1	1	4	0	0	3	1	1	0
.....												
89	116581.	0.5	12	2	1	4	1	1	3	1	1	0
89	116581.	1.5	12	2	1	4	1	1	3	1	1	0
89	116581.	2.5	12	2	1	4	1	1	3	1	1	0
90	116625.	1.5	12	2	1	2	2	1	3	1	1	0
90	116625.	2.5	12	2	1	2	2	1	3	1	1	0
== Ionization potentials ==												
1	117345.								3	1	1	
2	132660.								1	2	1	

Two separate models are used. These are: the model of calculation of the atomic lines parameters without regard to multiplet structure, and with regard to multiplet structure.

Two local databases are created as the result of applications of these two models. The first one contains parameters of the multiplets, and second one contains parameters of components of the multiplets. The algorithm of the calculation of the multiplets parameters and the example of such calculations are presented below. Note that the computing methods provide the following lines parameters: wave number of the line centre ( $\omega_0$ ), oscillator strength of optically allowed jump, half-width the of atomic line ( $\gamma$ ), statistical weight of the lower energetic state ( $g$ ).

## 6.1 The algorithm of calculation of the multiplets parameters

### *Step 1: Formation of the local database of terms*

The calculations of energies and statistical weights of atomic terms is performed under the following formulas:

$$E_j = \sum_{i \in j} E_i (2J_i + 1) \frac{1}{\sum_{i \in j} (2J_i + 1)}, \quad g_j = \sum_{i \in j} (2J_i + 1) \quad (1)$$

where  $E_i$  is the energy of  $i$ -th components of  $j$ -th atomic term;  $J_i$  is the total angular momentum quantum number of the  $i$ -th components of the  $j$ -th atomic term;  $E_j$  is the energy of  $j$ -th atomic term.

### *Step 2: Sorting of the atomic terms*

The terms provide a spectral series, if at identical values of quantum numbers  $l, L, S, \pi, L'', S'', \pi''$  the principal quantum number  $n$  is changed. The separate groups of the terms are formed from the terms of ground (non-excited) states.

### *Step 3: The atomic line parameters*

The purpose of the following step of the calculation algorithm is to identify the nomenclature of atomic lines, numbers of the bottom and lower energetic states, wave numbers of the lines centres, and the energy of the lower states.

In order to choose the quantum transition (from the full set of quantum transitions), which result in formation of spectral lines, it is necessary to use specific rules of selection. Algorithmically this is simple



searching through all allocated terms  $i$ , it is then necessary to analyse consistently all another terms  $j$ . For the dipole one-electronic transitions  $i \rightarrow j$ , formation of a spectral line is possible if constrained by the following conditions [60–62]:

$$l_j = l_i \pm 1; \quad S_j = S_i; \quad (2)$$

$$n_j > n_i \quad (\text{this check fixes calculation of lines in absorption});$$

$$\pi_j \neq \pi_i \quad (\text{the parity of the states should change}); \quad (3)$$

$$L_j = L_i, \quad L_j = L_i \pm 1; \quad L_j \neq L_i, \text{ if } L = 0; \quad (4)$$

$$S_j'' = S_i''; L_j'' = L_i''; \pi_j'' = \pi_i'', \quad (5)$$

where  $L$  is the quantum number of the total orbital angular momentum;  $l$  is the orbital angular momentum quantum number;  $S$  is the total spin angular momentum quantum number;  $\pi$  is the parity of the state; ( )'' denotes quantum numbers of the parent terms.

The last three conditions correspond to the requirement of the parent terms preservation. The rules of selection (2)–(5) should not be checked in that case, when one of the terms is formed by a configuration of equivalent electrons.

At quantum transitions from the atoms and ions ground states the resulting ion can be formed as in ground states and in excited states. The probability of such a condition is determined by the genealogical factors [60, 61].

If the specified rules of selection is satisfied for a given transition, then the next line in a local database of the atomic lines parameters is added, and thus the wave number, energy and statistical weight of the lower level of the line is fixed. In this database the additional attributes of filling of the internal atomic shell, and the attribute of equivalence of the optical electron are entered for each line.

#### ***Step 4: Calculation of the multiplet strength***

The multiplet strength is calculated by the formula [60, 61]:

$$S(\alpha SL; \alpha' SL') = s(\alpha SL; \alpha' SL') R^2(nl; n'l'), \quad (6)$$

where  $s$  is the multiplet strength factor;  $R^2$  is the one-electronic radial integral square.

#### ***Step 5: Calculation of the multiplet strength factor***

The following three cases are taken into account:

(a) one electron outside of a filled shell:

$$s = 2l_{\max}, \quad l_{\max} = \max\{l, l'\}; \quad (7)$$

(b) one electron outside of a non-filled shell:

$$s = (2S + 1)(2L + 1)(2L' + 1)W^2(l, l', L, L'; 1, L'') \cdot l_{\max}; \quad (8)$$

(c)  $q \neq 1$  equivalent electrons outside of a non-filled shell:

$$s(\alpha SL; \alpha' SL') = (2S+1)(2L+1)(2L'+1) \cdot W^2(l, l', L, L'; 1, L'') \cdot l_{\max} q \left| G_{S''L''}^{SL} \right|^2. \quad (9)$$

Here  $W^2$  is the square of the Racah factors.

### Step 6: Calculation of the genealogical factors

The values of the genealogical factors are defined by initial and final configurations of given quantum transition, and also by the model of vector connection for the atom in initial and final configurations. The model of the  $LS$ -coupling is a variant of the computing system. Values of the genealogical factors for quantum transitions are tabulated (see, for example, Table 6.2). The FORTRAN-code developed by R. Zare [56] was also used for these calculations.

**Table 6.2: Example of the genealogical factors**

1. Transition from state  $p^2$  ( $l = 1, q = 2$ )

$G_{S''L''}^{SL}$			
Initial configuration $p^2(2S+1L)$	Final configuration $p(2S''+1L'')$		
	$^2P$	—	—
$^1S$	1		
$^3P$	1		
$^1D$	1		

2. Transition from state  $p^1 - s^1$ :  $s = 2l_{\max}$

3. Transition from state  $p^3$  ( $l = 1, q = 3$ )

$G_{S''L''}^{SL}$			
Initial configuration $p^3(2S+1L)$	Final configuration $p^2(2S''+1L'')$		
	$^1S$	$^3P$	$^1D$
$^4S$	0	1	0
$^2P$	2/9	1/2	5/18
$^2D$	0	1/2	1/2

4. Transition from state  $p^4$  ( $l=1, q=4$ )

$G_{S''L''}^{SL}$			
Initial configuration $p^4(2S+1L)$	Final configuration $p^3(2S''+1L'')$		
	$^4S$	$^2P$	$^2D$
$^1S$	0	1	0
$^3P$	1/3	1/4	5/12
$^1D$	0	1/4	3/4

5. Transition from state  $p^5$  ( $l=1, q=5$ )

$G_{S''L''}^{SL}$			
Initial configuration $p^5(2S+1L)$	Final configuration $p^4(2S''+1L'')$		
	$^1S$	$^3P$	$^1D$
$^2P$	1/15	3/5	1/3

## 6.2 Calculation of the one-electronic radial integrals

For the calculation of the one-electronic radial integrals the Bates and Damgaard method [63] is used. The accuracy of this method is sufficient for the solution of radiation heat transfer and radiative gas dynamics problems.

One can assume that the calculation of radial integral is possible by neglecting a deviation of atom's (or ion's) potential from its asymptotic (Coulomb) form. Then the exact equation for radial wave function  $R$

$$\frac{d^2R}{dr^2} + \left[ 2U(r) - \frac{l(l+1)}{r^2} - E \right] R = 0 \quad (10)$$

may be replaced by the following approximate equation:

$$\frac{d^2R}{dr^2} + \left[ 2\frac{z}{r} - \frac{z^2}{(n^*)^2} - \frac{l(l+1)}{r^2} \right] R = 0, \quad (11)$$

where  $U$  is the actual potential of the atom;  $E$  is the energy of the given term;  $z$  is the residual charge ( $z=1$  for a neutral atom);  $n^*$  is the effective principal quantum number. Here the atomic units are used, and the energy is measured in  $Ry$ .

The effective quantum number  $n^*$  is defined as follows:  $n^* = z/\sqrt{E_n}$ , where  $E_n$  is the energy of  $n$ -th level [58].

The value of the square of one-electronic radial integral is defined under the following formulas:

$$R^2 = \frac{2l_{\max}}{4l_{\max}^2 - 1} \sigma^2, \quad \sigma = \frac{1}{\sqrt{4l_{\max} - 1}} \int_0^\infty R_j R_i r dr. \quad (12)$$

To simplify these calculations the following functions  $F(n^*, l)$ ,  $F(n_{l-1}^*, n_l^*, l)$  were introduced and tabulated in Ref. [63]. Then the calculations of the radial integrals are performed under the following formula:

$$\sigma = \sigma(n_{l-1}^*, l-1; n_l^*, l; z) = \frac{1}{z} F(n^*, l) F(n_{l-1}^*, n_l^*, l). \quad (13)$$

But the calculations of the radial integrals can also be performed without using of the Bates and Damgaard Tables. The Schrodinger equation with effective potential is easily solving with using the finite-difference methods presented below.

For the numerical solution of the Schrodinger equation and the Hartree–Fock equations, the Numerov method [64] is used as one possibility. This method has a 4th order of approximation and is applied to the solution of the wave equation. However it is known, that Equation (10) cannot be solved directly for the whole calculated area. The missing solution may be obtained at  $r \rightarrow \infty$ . In order to prevent this, the equation is solved at first from the point  $r=0$  up to some intermediate value  $r^*$ . Then the equation is solved from the right border of calculated area up to that point. Then the solutions are tied together in the point  $r^*$  using some normalising procedure. The algorithm of the solution of the problem is presented in detail in Ref. [64].

Another algorithm of the solution was used in the paper. This algorithm is based on the time-relaxation method. According to this method the solution of the initial differential equation is replaced by the solution of the appropriate unsteady equation at asymptotic conditions to time approaching infinity. For this purpose the imaginary non-stationary can be summed into the Equation (11):

$$\frac{\partial R}{\partial t} + \left( \frac{\alpha}{r^2} - \frac{\gamma}{r} - \beta \right) R = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right), \quad (14)$$

where  $\alpha = l(l+1)$ ,  $\beta = 2\varepsilon = -\frac{1}{n^{*2}}$ ,  $\gamma = 2z$ .

The boundary conditions for the solution of Equation (14) are as follows:

$$r = r_{\min} = 0, \quad R = 0; \quad r = r_{\max} \rightarrow \infty, \quad R = 0.$$

The size  $r_{\max}$  is defined with a large arbitrariness. The computing experiments show that, as a rule, it is sufficient to input

$$r_{\max} - r_2 = (3 \div 5)(r_2 - r_1),$$

where  $r_1, r_2$  are the co-ordinates of the turn points (co-ordinates of the potential curve at the given value of the energy  $E$ ).

For the calculations of the radial wave integrals this condition must be altered, so that

$$r_{\max} - \max\left(r_2^{(f)}, r_2^{(f)}\right) = (3 \div 5) \left[ \max\left(r_2^{(f)}, r_2^{(f)}\right) - \min\left(r_1^{(b)}, r_1^{(b)}\right) \right],$$

where  $b$  and  $f$  are the indexes of energy states for which the wave function is determined.

For initial conditions the analytical solution of the Equation (14) for the harmonic potential may be used.

A finite-difference analogue of the Equation (14) may be solved by any computational method (for example, by the Thomas algorithm). This method does not have problems with functions calculated in the adjacent regions.

### 6.3 Description of created databases

#### 6.3.1 Local databases of the atomic lines parameters

The general result of the calculation of atomic and ions lines parameters is the formation of the local database of all atomic lines parameters. Example of such database for lines of atom N as listed in Table 6.3. Each line in the table corresponds to the fixed atomic line. For each line the following parameters are given:

- $E$  is the energy of the lower level,  $\text{cm}^{-1}$ ;
- $OMEGA$  is the wavenumber of the line centre,  $\text{cm}^{-1}$ ;
- $g$  is the statistical weight of the lower level;
- $f$  is the absorption oscillator strength;
- $C_4$  is the Stark square-law effect constant.

It is also assumed that the broadening of atomic lines can be calculated by a nonadiabatic approximation, while the broadening of ions lines can be calculated in adiabatic one.

**Table 6.3: Atomic lines parameters**

Atom: N			Nlines = 1706	
.....E.....:OMEGA:.....g....f:.....:C4....				
0.0	83285.5	4.00	0.011401	0.05576
0.0	83319.3	4.00	0.022802	0.06000
0.0	83366.0	4.00	0.034203	0.03219
0.0	103618.1	4.00	0.001318	0.23133
0.0	103668.1	4.00	0.002635	0.25417
0.0	103736.8	4.00	0.003953	0.20102
0.0	109813.5	4.00	0.000427	0.00463
0.0	109857.8	4.00	0.000854	0.00463
0.0	109927.9	4.00	0.001281	0.00463
0.0	112565.9	4.00	0.000205	0.00463
0.0	112610.6	4.00	0.000410	0.00463
0.0	112682.6	4.00	0.000615	0.00463
0.0	114015.0	4.00	0.000142	0.00463
0.0	114072.0	4.00	0.000283	0.00463
0.0	114146.0	4.00	0.000425	0.00463
0.0	114809.0	4.00	0.000142	0.00463
0.0	114890.0	4.00	0.000283	0.00463
0.0	114942.0	4.00	0.000425	0.00463
0.0	115483.0	4.00	0.000142	0.00463
0.0	115483.0	4.00	0.000283	0.00463

0.0	115483.0	4.00	0.000425	0.00463
0.0	115855.0	4.00	0.000142	0.00463
0.0	115855.0	4.00	0.000283	0.00463
0.0	115855.0	4.00	0.000425	0.00463
0.0	116124.0	4.00	0.000142	0.00463
0.0	116124.0	4.00	0.000283	0.00463
0.0	116124.0	4.00	0.000425	0.00463
0.0	116312.0	4.00	0.000142	0.00463
0.0	116312.0	4.00	0.000283	0.00463
0.0	116312.0	4.00	0.000425	0.00463
0.0	104864.0	4.00	0.016263	0.20190
0.0	104890.0	4.00	0.032526	0.28639
0.0	104957.0	4.00	0.048789	0.23444
0.0	110325.0	4.00	0.003346	0.00463
0.0	110351.0	4.00	0.006692	0.00463
0.0	110403.0	4.00	0.010038	0.00463
0.0	112855.0	4.00	0.001154	0.00463
0.0	112874.0	4.00	0.002309	0.00463
0.0	112912.0	4.00	0.003463	0.00463
0.0	114259.0	4.00	0.007500	0.00463
0.0	114259.0	4.00	0.015000	0.00463
-----				
.....E.....:OMEGA:....g....f:.....:C4.....				
-----				
0.0	114274.0	4.00	0.022500	0.00463
0.0	115103.0	4.00	0.007500	0.00463
0.0	115103.0	4.00	0.015000	0.00463
0.0	115103.0	4.00	0.022500	0.00463
0.0	115618.0	4.00	0.007500	0.00463
0.0	115618.0	4.00	0.015000	0.00463
0.0	115618.0	4.00	0.022500	0.00463
0.0	115990.0	4.00	0.007500	0.00463
0.0	115990.0	4.00	0.015000	0.00463
0.0	115990.0	4.00	0.022500	0.00463
0.0	116259.0	4.00	0.007500	0.00463
0.0	116259.0	4.00	0.015000	0.00463
0.0	116259.0	4.00	0.022500	0.00463
0.0	116441.0	4.00	0.007500	0.00463
0.0	116441.0	4.00	0.015000	0.00463
0.0	116441.0	4.00	0.022500	0.00463
0.0	116581.0	4.00	0.007500	0.00463
0.0	116581.0	4.00	0.015000	0.00463
0.0	116581.0	4.00	0.022500	0.00463
19223.0	67000.2	6.00	0.036349	0.05652
19231.0	66900.4	4.00	0.030291	0.05576
19231.0	66992.2	4.00	0.006058	0.06000
19223.0	85004.4	6.00	0.005050	0.25069
...				
107447.2	7655.8	4.00	0.003861	0.78424
107447.2	8170.8	4.00	0.000583	0.78424
107447.2	8170.8	4.00	0.001166	0.78424
107447.2	8170.8	4.00	0.001749	0.78424
107447.2	8542.8	4.00	0.000583	0.78424
107447.2	8542.8	4.00	0.001166	0.78424
107447.2	8542.8	4.00	0.001749	0.78424
107447.2	8811.8	4.00	0.000583	0.78424
107447.2	8811.8	4.00	0.001166	0.78424
107447.2	8811.8	4.00	0.001749	0.78424
107447.2	8993.8	4.00	0.000583	0.78424
107447.2	8993.8	4.00	0.001166	0.78424
107447.2	8993.8	4.00	0.001749	0.78424
107447.2	9133.8	4.00	0.000583	0.78424
107447.2	9133.8	4.00	0.001166	0.78424
107447.2	9133.8	4.00	0.001749	0.78424

### 6.3.2 The database of the atoms and ions energy levels characteristics

The database is listed in Table 6.1. This database is generated on the basis of the Ref. [58]. Here for each component of a multiplet (the line in the table) the following is listed:

No is the level serial number;

$E(n,l)$  is the energy of the multiplet component;

$J$  is the total angular momentum quantum number;

$n$  is the principal quantum number;

$l$  is the orbital quantum number;

$q$  is the number of equivalent electrons;

$\#S$  is the multiplicity of the term  $2S + 1$ , where  $S$  is the total spin angular momentum;

$L$  is the quantum number of the total orbital angular momentum;

$\pi$  is the attribute of the parity of the term;

$\#S''$  is the multiplicity of the parental term;

$L''$  is the quantum number of the total orbital angular momentum of the parental term;

$\pi''$  is the attribute of parity of the parental term;

$sh$  is the attribute of the shifted term.

At the end of each file the following data concerning given parental terms are listed:

$N$  is the number of the parental term;

$E(n,l)$  is the energy of the parental term;

$S$  is the multiplicity of the parental term;

$L$  is the quantum number of the total orbital angular momentum of the parental term;

$\pi''$  is the attribute of parity of the parental term.

## 7.0 SPECTRAL EMISSIVITY OF STRONG SHOCK WAVES

As an example of the use of the models analyzed above, the hybrid radiative-collisional model of the plasma kinetics behind strong shock waves in air and in  $\text{CO}_2\text{-N}_2$  mixtures is considered in the Chapter. Separate parts of the model were presented by the author in previous publications [21–24, 65]. It should be a specially stressed that models analyzed in [1, 66–74] had a beneficial influence on the author concepts and biases towards such a model. There is a need to refer also some new and efficient models recently published [19, 27].

In this model the shock wave front is treated as discontinuity, and the relaxation processes behind this front are studied. It is well known that this simplest gasdynamic model allows study physical-chemical kinetics behind shock wave fronts in wide region of parameters. This model contains several blocks: the gas dynamics part, the chemical kinetics part, the physical kinetics part and the radiation part. Characteristic feature of the model is: it is assumed that the Boltzmann distribution of molecules at lower vibrational levels would not be significant disturbed, so we can introduce vibrational temperature of molecules. Electronic states of atoms, molecules and ions are proposed as equilibrium in one variant of the model, and they are assumed as nonequilibrium in another variant of the model. Temperatures of all heavy particles are assumed to be the same (in the first model) and differ from temperature of electrons and vibrational temperature. Only few electronic levels of diatomic molecules are considered as separate quasi-particles in the list of species, which are taken into account in total scheme of physical-chemical processes. To describe excitation and de-activation of the states the Radiative-collisional model was used.

This hybrid model of multi-temperature chemical kinetics and radiation is applied to study of air shock waves for typical super orbital re-entry conditions (velocities  $11 \div 14$  km/s and pressures  $20 \div 4400$  erg/cm<sup>3</sup>), and also to study relaxation processes behind shock waves in CO<sub>2</sub>–N<sub>2</sub> mixtures. In the last case the analysis of several experimental data is presented.

## 7.1 Model description

The plane shock in air and CO<sub>2</sub>–N<sub>2</sub>–Ar mixtures is considered. It is assumed that values of pressure, density, translational temperature of heavy particles and velocity of gas are changes abruptly by the passage of the shock wave front ( $x_0 = 0$ ) but the initial molar fraction of species  $x_{i,0}$ , the temperature of electrons and the vibrational temperature  $T_{v,i,0}$  don't change. The mixture formed behind the shock wave front consists eleven species for air (N<sub>2</sub>, O<sub>2</sub>, NO, N, O, N<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup>, NO<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, e<sup>-</sup>) and twenty eight species for CO<sub>2</sub>–N<sub>2</sub> mixture (C<sub>2</sub>, CN, CO, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, NO, Ar, N, O, CO<sup>+</sup>, N<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup>, NO<sup>+</sup>, C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, e<sup>-</sup>, CN(*B*<sup>2</sup>Σ), CN(*A*<sup>2</sup>Π), C2(*d*<sup>3</sup>Π), CO(*A*<sup>1</sup>Π), CO(*B*<sup>1</sup>Σ), CO(*b*<sup>3</sup>Σ), CO(*a*<sup>3</sup>Π), N<sub>2</sub>(*A*<sup>3</sup>Σ), N<sub>2</sub>(*B*<sup>3</sup>Π), NO(*A*<sup>2</sup>Σ), *hν*).

Governing equations for determination of gas parameters behind the shock wave have the following form:

$$\frac{d}{dx}(\rho u) = 0, \quad \frac{d}{dx}(p + \rho u^2) = 0, \quad \frac{d}{dx}\left(h + \frac{u^2}{2}\right) = 0, \quad (1)$$

where

$$p = \frac{\rho R_0 T}{M_\Sigma} = nkT, \quad M_\Sigma = \sum_{i=1}^N \mu_i x_i, \quad \mu_i = m_i N_A, \quad (2)$$

$$h = \left[ (T - T^0) \left( \frac{5}{2} + \sum_{i=1}^{N_M} x_i \right) + \sum_{i=1}^{N_M} x_i \sum_{j=1}^{N_{V,i}} g_{i,j} \frac{\theta_{i,j}}{\exp(\theta_{i,j}/T_{v,i}) - 1} + \sum_{i=1}^{N_\epsilon} \Delta_f H_i^0 x_i \right] \frac{R_0}{M_\Sigma}, \quad (3)$$

where  $\rho, u, p$  are the density, velocity and pressure;  $T, h$  are the translational temperature and enthalpy;  $x_i$  is the molar fraction of  $i$ -th chemical components;  $m_i$  is the mass of  $i$ -th component;  $k, N_A$  are the Boltzmann and the Avogadro constants;  $R_0$  is the universal gas constant;  $\theta_{i,j}$  is the characteristic vibrational temperature of the  $j$ -th vibrational mode of  $i$ -th molecular species (see Table 7.1);  $g_{i,j}$  is the degeneration of the  $j$ -th vibrational mode;  $N_M$  is the number of molecular species (in the case under consideration all molecular species are the diatomic or linear three-atomic (CO<sub>2</sub>) molecules);  $T_{v,i}$  is the vibrational temperature for  $i$ -th molecular species;  $N_{V,i}$  is the number of vibrational modes for the  $i$ -th molecule. All functions before the shock wave front ( $x_0 = 0$ ) are marked by zero-symbol. It is assumed that all functions are given in undisturbed gas before the shock wave front ( $\rho_0, u_0, p_0, h_0, T_0, T_{v,i,0}, x_{i,0}$ ).

**Table 7.1: Characteristic vibrational temperatures and dissociation energy of molecular species**

$\theta_v, K$						
N <sub>2</sub>	O <sub>2</sub>	NO	CO	CO <sub>2</sub>		
				Symmetric mode	Deformation mode	Anti-symmetric mode
3396.	2230.	2690.	3080.	959.	1920.	3383.
$D_i, K$						
113200.	59380.	75500.	129000.	65930.		



Equation (1) is integrated step-by-step in the line of  $x$  from  $x=0$ . At the beginning of each computational step up  $x$ -axis the molar-volume concentrations  $x_i$  are calculated with the use of the following chemical kinetics equations:

$$\frac{dX_k}{dt} = \sum_{j=1}^{N_R} \left[ (b_{k,j} - a_{k,j}) k_j^f \prod_{i=1}^{11} X_i^{a_{ij}} + (a_{k,j} - b_{k,j}) k_j^r \prod_{i=1}^{11} X_i^{b_{ij}} \right], \quad k=1,2,\dots,11. \quad (4)$$

The list of chemical reactions:

$$\sum_{i=1}^N a_{i,j} [X_i] \xrightleftharpoons[k_j^r]{k_j^f} \sum_{i=1}^N b_{i,j} [X_i], \quad j=1,2,\dots,N_R, \quad (5)$$

where  $[X_i]$  are the symbol of  $i$ -th species,  $a_{i,j}, b_{i,j}$  are the stoichiometric coefficients. List of the chemical reactions started from kinetic models suggested in [2] for air, and in [3] for  $\text{CO}_2\text{-N}_2\text{-Ar}$  mixtures. Analysis of the kinetic models on the examples of Earth and Martians spacecraft entries, and some their modifications were recently discussed in [75, 76].

Rate coefficients of the forward and reverse chemical reactions, as well as the constants of equilibrium chemical reactions are used in the generalized Arrhenius form:

$$k_i^f = A_i^f T^{B_i^f} e^{-\frac{T_i^f}{T}}, \quad k_i^r = A_i^r T^{B_i^r} e^{-\frac{T_i^r}{T}}, \quad K_i = \frac{k_i^f}{k_i^r}, \quad K = A_{eq} T^{B_{eq}} e^{-\frac{T_{eq}}{T}}. \quad (6)$$

Values of  $A_i^r$  and  $B_i^r$  ( $T_i^r=0$ ) for associative ionization reactions are borrowed from [1] and those for electron-impact ionization reactions from [77] (as in [1], values of the parameters for the electron-impact ionization reactions are assumed to be the same). Then values of  $A_i^f$ ,  $B_i^f$  and  $T_i^f$  are calculated according to (4). Though only one of the particles involved in forward or reverse reaction is electron the value of  $T_e$  is used instead of  $T$  for the calculation of corresponding reaction rate coefficient [77,78].

The relaxation equations for vibrational energy are written in the form [68, 25]:

$$\frac{de_m}{dt} = Q_{VT}^m + Q_{VV}^m + Q_{CV}^m, \quad (7)$$

where

$$Q_{VT}^m = \frac{e_m^0 - e_m}{\tau_m}, \quad \tau_m = \left( \sum_{i=1}^N \frac{x_i}{\tau_{m,i}} \right)^{-1},$$

$$Q_{VV}^m = k_{m,n} \left[ e_n (e_m + 1) \exp\left(\frac{\theta_n}{T} - \frac{\theta_m}{T}\right) - e_m (e_n + 1) \right],$$

$$Q_{CV}^m = \frac{1}{X_i} \sum_{j=1}^{N_R} (e_{mj} - e_m) \left( \frac{dX_m}{dt} \right)_j, \quad e_m = \frac{1}{\exp(\theta_m/T_{v,m}) - 1}, \quad (8)$$

$e_m$  is the average number of  $m$ -th type vibrational quanta rated per one molecule;  $T_{v,m}$  is the vibrational temperature;  $e_m^0$  is the equilibrium value  $e_m$ ;  $\tau_{m,i}$  is the vibrational VT-relaxation time for  $m$ -th molecule in collisions with  $i$ -th particles;  $Q_{vT}^m, Q_{vv}^m, Q_{cv}^m$  are the vibrational energy sources (or sinks) due to the vibrational-translation (VT), the vibrational-vibration VV, and the dissociative-vibration interaction (CV).

Several models of VV-, VT-, and CV-relaxations were used in the hybrid kinetic model under consideration. The kinetic model of VV- relaxation for air takes into account vibrational energy exchange for  $N_2$  and  $O_2$  molecules:

$$\tau_{m,i} = \alpha_{m,i} \left( \frac{T_e}{10^4} \right)^{n_{m,i}} \frac{\exp\left(\frac{\beta_{m,i}}{T_e^{1/3}}\right)}{p}, \quad k_{m,n} = k_{10}^{01} = 0.0651 \left( \frac{10^4}{T} \right)^{0.77} \frac{\exp\left(\frac{64.5}{T^{1/3}}\right)}{p}, \quad (9)$$

where  $k_{10}^{01}$  is the rate coefficient of VV-exchange reaction for the following reaction  $N_2(V_1=1) + O_2(V_2=0) \rightarrow N_2(V_1'=0) + O_2(V_2'=1)$ ;  $e_{mj}$  is the average number of vibrational quanta per one molecule lost (or gained) by the  $m$ -th molecules through each of the  $j$ -th chemical reaction.

The kinetic model of VV-relaxation for  $CO_2$ - $N_2$ -Ar mixtures takes into account vibrational energy exchange for  $CO_2$ ,  $N_2$ ,  $CO$ :

$$Q_{vv}^m = \sum_n^{N_V} k_{m,n} F_{m,n}, \quad F_{m,n} = \frac{r}{g_m} \left[ e_n^q (e_m + 1)^r \exp\left(\frac{q\theta_n}{T} - \frac{r\theta_m}{T}\right) - e_m^r (e_n + 1)^q \right],$$

$$k_{m,n} = \sum_l^{n_c} x_l (k_{m,n})_l, \quad (10)$$

where  $k_{m,n}$  is the rate constants of the VV-exchange between the  $m$ -th and  $n$ -th vibrational modes;  $(k_{m,n})_l$  is the rate constant for the  $l$ -th type of the vibrational exchange reaction;  $g_m$  is the degeneracy of the  $m$ -th energy level. It is assumed that  $r$  quanta of the  $m$ -th level exchanges with  $q$  quanta of the  $n$ -th level. Rate constants of the reverse processes  $k_{n,m}$  were calculated according to the detailed balance principle

$$k_{n,m} = k_{m,n} \exp\left(\frac{q\theta_n}{T} - \frac{r\theta_m}{T}\right). \quad (11)$$

The coefficients of the VV-relaxation  $k_{m,n}$  were presented in the following form:

$$k_{m,n}^{-1} = \tau_{VV}, \quad p\tau_{VV} = \exp\left(A_{VV} + B_{VV} \frac{1}{T^{1/3}} + C_{VV} \frac{1}{T^{2/3}} + D_{VV} T^{1/3}\right), \quad (12)$$

and borrowed from [79]. These data are presented in Table 7.2 ( $p\tau$  in atm·s). Some constants were chosen in accordance with recommendations of [80–84].

**Table 7.2: List of the VV-reactions and corresponding approximation constants**

				$A_{VV}$	$B_{VV}$	$C_{VV}$	$D_{VV}$
1	$\text{CO}_2\_V3 + \text{CO}_2$	$\Rightarrow$	$\text{CO}_2\_V1 + \text{CO}_2$	-26.85	173.22	-539.74	0.09645
2	$\text{CO}_2\_V3 + \text{N}_2$	$\Rightarrow$	$\text{CO}_2\_V1 + \text{N}_2$	-33.65	274.41	-886.56	0.18433
3	$\text{CO}_2\_V3 + \text{CO}$	$\Rightarrow$	$\text{CO}_2\_V1 + \text{CO}$	-15.52	37.79	-104.90	0.
4	$\text{CO}_2\_V3 + \text{O}_2$	$\Rightarrow$	$\text{CO}_2\_V1 + \text{O}_2$	-23.13	136.11	-395.78	0.03406
5	$\text{CO}_2\_V3 + \text{O}$	$\Rightarrow$	$\text{CO}_2\_V1 + \text{O}$	-15.90	-99.11	-686.00	0.00078
6	$\text{CO}_2\_V3 + \text{CO}_2$	$\Rightarrow$	$\text{CO}_2\_V2 + \text{CO}_2$	-26.85	173.22	-539.74	0.09645
7	$\text{CO}_2\_V3 + \text{N}_2$	$\Rightarrow$	$\text{CO}_2\_V2 + \text{N}_2$	-33.65	274.41	-886.56	0.18433
8	$\text{CO}_2\_V3 + \text{CO}$	$\Rightarrow$	$\text{CO}_2\_V2 + \text{CO}$	-15.52	37.79	-104.90	0.
9	$\text{CO}_2\_V3 + \text{O}_2$	$\Rightarrow$	$\text{CO}_2\_V2 + \text{O}_2$	-23.13	136.11	-395.78	0.03406
10	$\text{CO}_2\_V3 + \text{O}$	$\Rightarrow$	$\text{CO}_2\_V2 + \text{O}$	-15.90	-99.11	-686.00	0.00078
11	$\text{CO}_2\_V3 + \text{CO}$	$\Rightarrow$	$\text{CO}_2 + \text{CO\_V}$	-23.28	94.73	-301.21	0.06858
12	$\text{N}_2\_V + \text{CO}_2$	$\Rightarrow$	$\text{N}_2 + \text{CO}_2\_V3$	-22.25	-123.36	2396.73	0.14764
13	$\text{N}_2\_V + \text{CO}_2$	$\Rightarrow$	$\text{N}_2 + \text{CO}_2\_V1$	-8.14	-80.08	451.33	0.
14	$\text{N}_2\_V + \text{CO}_2$	$\Rightarrow$	$\text{N}_2 + \text{CO}_2\_V2$	-8.14	-80.08	451.33	0.
15	$\text{N}_2\_V + \text{CO}$	$\Rightarrow$	$\text{N}_2 + \text{CO\_V}$	-18.04	71.29	-266.51	0.002
16	$\text{CO\_V} + \text{CO}_2$	$\Rightarrow$	$\text{CO} + \text{CO}_2\_V1$	-8.14	-80.08	451.33	0.
17	$\text{CO\_V} + \text{CO}_2$	$\Rightarrow$	$\text{CO} + \text{CO}_2\_V2$	-8.14	-80.08	451.33	0.
18	$\text{CO\_V} + \text{NO}$	$\Rightarrow$	$\text{CO} + \text{NO\_V}$	-34.61	166.27	333.4	0.316

Remark for Table 7.2: V1, V2, V3 are the symmetrical, deformation and anti-symmetrical modes of the  $\text{CO}_2$  molecules.

The times of the VT-relaxation were presented in the following form (in accordance with recommendations [1]):

$$\tau = \tau_{VT} + \frac{1}{N_t \sigma_V \sqrt{8kT/(\pi M_m)}}, \quad \sigma_V = \sigma'_V (50000/T)^2, \quad (13)$$

$$p\tau_{VT} = \exp \left[ A_{VT} \left( T^{-1/3} - B_{VT} \right) - 18.42 \right], \text{ atm}\cdot\text{s}, \quad (14)$$

were the approximation coefficients  $A_{VT}, B_{VT}, \sigma'_V$  are presented in Table 7.3 (these data were borrowed from [1]);  $N_t$  is the total number density of a gas mixture,  $\text{cm}^{-3}$ ;  $k$  is the Boltzmann constant;  $M_m$  is the mass of the  $m$ -th molecule.

**Table 7.3: List of the VT-reactions and corresponding approximation coefficients**

				$A_{VT}$	$B_{VT}$	$\sigma'$					$A_{VT}$	$B_{VT}$	$\sigma'$
1	$\text{CO}_2\text{-V1} + \text{CO}_2 \Rightarrow \text{CO}_2 + \text{CO}_2$			36.5	-0.0193	$10^{-16}, \text{cm}^2$	19	$\text{CO}_2\text{-V3} + \text{O} \Rightarrow \text{CO}_2 + \text{O}$			37.6	0.0278	$3 \times 10^{-17}, \text{cm}^2$
2	$\text{CO}_2\text{-V1} + \text{N}_2 \Rightarrow \text{CO}_2 + \text{N}_2$			45.4	0.0305		20	$\text{CO}_2\text{-V3} + \text{N} \Rightarrow \text{CO}_2 + \text{N}$			35.8	0.0271	
3	$\text{CO}_2\text{-V1} + \text{CO} \Rightarrow \text{CO}_2 + \text{CO}$			45.4	0.0305		21	$\text{CO}_2\text{-V3} + \text{AR} \Rightarrow \text{CO}_2 + \text{AR}$			50.3	0.0321	
4	$\text{CO}_2\text{-V1} + \text{C} \Rightarrow \text{CO}_2 + \text{C}$			33.7	0.0263		22	$\text{N}_2\text{-V} + \text{CO}_2 \Rightarrow \text{N}_2 + \text{CO}_2$			245.	0.0305	
5	$\text{CO}_2\text{-V1} + \text{O} \Rightarrow \text{CO}_2 + \text{O}$			37.6	0.0278		23	$\text{N}_2\text{-V} + \text{N}_2 \Rightarrow \text{N}_2 + \text{N}_2$			221.	0.0290	
6	$\text{CO}_2\text{-V1} + \text{N} \Rightarrow \text{CO}_2 + \text{N}$			35.8	0.0271		24	$\text{N}_2\text{-V} + \text{CO} \Rightarrow \text{N}_2 + \text{CO}$			221.	0.0290	
7	$\text{CO}_2\text{-V1} + \text{AR} \Rightarrow \text{CO}_2 + \text{AR}$			50.3	0.0321		25	$\text{N}_2\text{-V} + \text{C} \Rightarrow \text{N}_2 + \text{C}$			72.4	0.0150	
8	$\text{CO}_2\text{-V2} + \text{CO}_2 \Rightarrow \text{CO}_2 + \text{CO}_2$			36.5	-0.0193		26	$\text{N}_2\text{-V} + \text{O} \Rightarrow \text{N}_2 + \text{O}$			72.4	0.0150	
9	$\text{CO}_2\text{-V2} + \text{N}_2 \Rightarrow \text{CO}_2 + \text{N}_2$			45.4	0.0305	$3 \times 10^{-18}, \text{cm}^2$	27	$\text{N}_2\text{-V} + \text{N} \Rightarrow \text{N}_2 + \text{N}$			180.	0.0262	$3 \times 10^{-18}, \text{cm}^2$
10	$\text{CO}_2\text{-V2} + \text{CO} \Rightarrow \text{CO}_2 + \text{CO}$			45.4	0.0305		28	$\text{N}_2\text{-V} + \text{AR} \Rightarrow \text{N}_2 + \text{AR}$			240.	0.0302	
11	$\text{CO}_2\text{-V2} + \text{C} \Rightarrow \text{CO}_2 + \text{C}$			33.7	0.0263		29	$\text{CO-V} + \text{CO}_2 \Rightarrow \text{CO} + \text{CO}_2$			218.	0.0305	
12	$\text{CO}_2\text{-V2} + \text{O} \Rightarrow \text{CO}_2 + \text{O}$			37.6	0.0278		30	$\text{CO-V} + \text{N}_2 \Rightarrow \text{CO} + \text{N}_2$			198.	0.0290	
13	$\text{CO}_2\text{-V2} + \text{N} \Rightarrow \text{CO}_2 + \text{N}$			35.8	0.0271		31	$\text{CO-V} + \text{CO} \Rightarrow \text{CO} + \text{CO}$			198.	0.0290	
14	$\text{CO}_2\text{-V2} + \text{AR} \Rightarrow \text{CO}_2 + \text{AR}$			50.3	0.0321		32	$\text{CO-V} + \text{C} \Rightarrow \text{CO} + \text{C}$			47.7	0.0500	
15	$\text{CO}_2\text{-V3} + \text{CO}_2 \Rightarrow \text{CO}_2 + \text{CO}_2$			36.5	-0.0193		33	$\text{CO-V} + \text{O} \Rightarrow \text{CO} + \text{O}$			47.7	0.0500	
16	$\text{CO}_2\text{-V3} + \text{N}_2 \Rightarrow \text{CO}_2 + \text{N}_2$			45.4	0.0305		34	$\text{CO-V} + \text{N} \Rightarrow \text{CO} + \text{N}$			47.7	0.0500	
17	$\text{CO}_2\text{-V3} + \text{CO} \Rightarrow \text{CO}_2 + \text{CO}$			45.4	0.0305		35	$\text{CO-V} + \text{AR} \Rightarrow \text{CO} + \text{AR}$			215.	0.0302	
18	$\text{CO}_2\text{-V3} + \text{C} \Rightarrow \text{CO}_2 + \text{C}$			33.7	0.0263								

Remark for Table 7.3: V1, V2, V3 are the symmetrical, deformation and anti-symmetrical modes of the  $\text{CO}_2$  molecules.

For recombination reactions the value  $e_{mj}$  is calculated as follows:

$$e_{mj} = \bar{e}_{mj} = \frac{D_m}{2\theta_m} - \frac{1}{2}. \quad (15)$$

For dissociation reactions the value  $e_{mj}$  was calculated in accordance with the model [68]:

$$e_{mj} = \frac{1}{\exp(\theta_m/T_F) - 1} - \frac{D_m/\theta_m}{\exp(\theta_m/T_F) - 1}, \quad T_F = \frac{1}{T_{m,n}} - \frac{1}{T} - \frac{1}{U}, \quad U = 3T, \quad (16)$$

where  $D_m$  is the dissociation energy.

The dissociation rate coefficients were calculated in accordance with the Merroun – Treanor model [68]:

$$k(T_v, T) = k^0(T) Z(T_v, T), \quad Z(T, T_v) = \frac{Q(T)Q(T_F)}{Q(T_v)Q(-U)}, \quad Q(T_\alpha) = \frac{1 - \exp(-D_0/T_\alpha)}{1 - \exp(-\theta/T_\alpha)},$$

$$T_\alpha = \{T, T_v, T_F, -U\}; \quad T_v < T, \quad (17)$$

where  $k_d^{(f,r),0}$  is the equilibrium dissociation rate coefficient. Formula (17) was used for dissociation reactions of  $C_2$ ,  $N_2$ ,  $O_2$ ,  $CN$ ,  $CO$ ,  $NO$ ,  $CO_2$  at collisions with other particles.

The electron energy conservation equation was integrated in the following form:

$$\frac{d}{dx} \left( \frac{3}{2} T_e n_e u \right) + T_e n_e \frac{du}{dx} = Q_{ei} + Q_{ea} + Q_{ai} + Q_{ion} + Q_{ev}, \frac{\text{erg} \cdot \text{cm}^3}{\text{sec}}, \quad (18)$$

where  $x$  is the distance from the shock wave front;  $T_e, n_e$  are the electronic temperature and volume concentration;  $Q_{ei}, Q_{ea}, Q_{ai}, Q_{ion}, Q_{ev}$  are the source (sink) terms in (18) which are considered below.

$$1) \quad Q_{ei} = 1.21 \times 10^{20} X_e X_i \frac{T - T_e}{T_e^{3/2}} \ln \Lambda \quad (19)$$

is the heating of the electrons at elastic electron-ion collisions;  $\ln \Lambda$  is the Coulomb logarithm;

$$2) \quad Q_{ea} = 3.378 \times 10^{10} X_e X_a \sqrt{T_e} (T - T_e) \left[ 1 - \left( 1 + \frac{T_e}{T_a^*} \right)^{-1} \right] \quad (20)$$

is the heating of the electrons at electron – neutral ( $a$ ) collisions ( $T_N^* = 31000\text{K}, T_O^* = 12000\text{K}$ );

$$3) \quad Q_{ai} = T \sum_{q=1}^3 \alpha_q k_q^f X_{a_q} X_{b_q} - T_e \sum_{q=1}^3 \beta_q k_q^r X_e X_{(a_q b_q)^+} \quad (21)$$

is the heating of electrons at association-ionization and dissociation-recombination reactions;  $\alpha_q, \beta_q$  are the coefficients of the energy transformation (these values were varied in the interval 0.05–0.1);  $k_q^f, k_q^r$  are the rate coefficients for the association and dissociation reactions; the following reactions are taken into account  $N + O \rightarrow NO^+ + e$ ,  $N + N \rightarrow N_2^+ + e$ ,  $O + O \rightarrow O_2^+ + e$ ,  $C + O \rightarrow C_2^+ + e$ ,  $C + N \rightarrow CN^+ + e$ ,  $C + O \rightarrow CO^+ + e$ ;

$$4) \quad Q_{ion} = -\gamma T k_{N,e}^f X_N X_e - \delta T k_{O,e}^f X_O X_e, \quad (22)$$

where  $k_{N,e}^f, k_{O,e}^f$  are the constants of impact electron-atom ionization; coefficients  $\gamma$  and  $\delta$  allow take into account state-by-state excitation of atomic levels subsequent and ionization (these coefficients are estimated by the value 0.1–1);

$$5) \quad Q_{ev} = 2 \times 10^{-16} \sum_V n_e n_V \omega_{e,V} P_{1,0,V} \cdot \left\{ \frac{\exp\left(-\frac{1.44\omega_{e,V}}{T_e}\right)}{\left[1 - \exp\left(-\frac{1.44\omega_{e,V}}{T_e}\right)\right]^2} - \frac{\exp\left(-\frac{1.44\omega_{e,V}}{T_v}\right)}{\left[1 - \exp\left(-\frac{1.44\omega_e}{T_v}\right)\right]^2} \right\}, \quad (23)$$

where  $Q_{ev}$  is the heating of the electrons at electron-vibrational interactions; index  $V$  denotes different vibrational modes, and probability of the vibrational transition is estimated as follows:

$$P_{1,0,V} = 0,45 \cdot 10^{-10} \exp\left(-\frac{10000}{T_e}\right). \quad (24)$$

Calculations of non-equilibrium spectral emissivity of heated air behind shock wave front were performed by the following model:

$$\varepsilon_{J',J''} = \left(\frac{16\pi^3 c}{3}\right) N_{J'} \omega_{J'J''}^4 \frac{S_{v'v''}}{(2 - \delta_{0,\Lambda'+\Lambda''})(2S+1)} \frac{S_{JJ''}}{(2J'+1)}, \frac{W}{\text{cm}^3 \cdot \text{sr}}. \quad (25)$$

or

$$\varepsilon_{J'J''} = 2.303 \times 10^{-23} N_{J'} \omega_{J'J''}^4 \frac{S_{v'v''}}{(2 - \delta_{0,\Lambda'+\Lambda''})(2S+1)} \frac{S_{JJ''}}{(2J'+1)}, \frac{W}{\text{cm}^3 \cdot \text{sr}}. \quad (26)$$

where

$$S_{v'v''} = (2 - \delta_{0,\Lambda'+\Lambda''})(2S+1) |R_{v'v''}|^2 \quad (27)$$

is the strength of vibronic radiation transfer,  $\text{cm}^{-1}$ ,  $S_{JJ''}$  is the strength of rotational line,  $\omega_{J'J''}$  is the wavenumber of rotational line,  $R_{v'v''}$  is the matrix element of vibronic transition,  $N_{J'}$  is the population of upper energy level.

Square of the matrix element of vibronic transition can be presented in the following form:

$$|R_{v'v''}|^2 = \frac{3h}{64\pi^4 a_0^2 e^2} \frac{2 - \delta_{0,\Lambda'}}{2 - \delta_{0,\Lambda'+\Lambda''}} \frac{1}{\omega_{v'v''}^3} \cdot A_{v'v''}, \quad (28)$$

where  $A_{v'v''}$  is the Einstein coefficient of vibronic transition.

And, finally, spectral emissivity in narrow spectral bands ( $\sim \Delta\omega \sim 10 \text{ cm}^{-1}$ ) were calculated by the formula

$$I_{\Delta\omega} = \sum_{v'} \sum_{J'} \varepsilon_{J'J''}, \quad (29)$$

To calculate a spectral radiation emissivity behind a shock wave front the “just overlapping line model” was also used [85]. The model was modified for calculation of the spectral emission coefficient (in  $\text{W}/(\text{cm}^3 \cdot \mu\text{m} \cdot \text{sr})$ ) of non-equilibrium radiation in electronic spectra of diatomic molecules

$$j_\lambda = 3.202 \times 10^{-10} \frac{N_{eel}}{Q_{vr} \lambda^6} \sum_{v'} \sum_{v''} \frac{S_{v'v''}}{|\Delta B_v|} \exp\left[-\frac{hc}{kT_v} E_{eel}(v')\right] \times \exp\left[-\frac{hc}{kT_r} \frac{B_{v'}}{\Delta B_v} (\omega - \omega_{v'v''} + B_{v'})\right], \quad (30)$$

were  $N_{eel}$  is the population of the excited electronic level,  $\text{cm}^{-3}$ ;  $\omega = 10000/\lambda$  is the wavenumber of a radiation,  $\text{cm}^{-1}$ ;  $\lambda$  is the wavelength of a radiation,  $\mu\text{m}$ ;  $\omega_{v'v''}$  is the wavenumber of electronic-vibrational transition,  $\text{cm}^{-1}$ ;  $\Delta B_v = B_{v'} - B_{v''}$ ;  $Q_{vr}$  is the statistical vibrational-rotational sum for the excited electronic

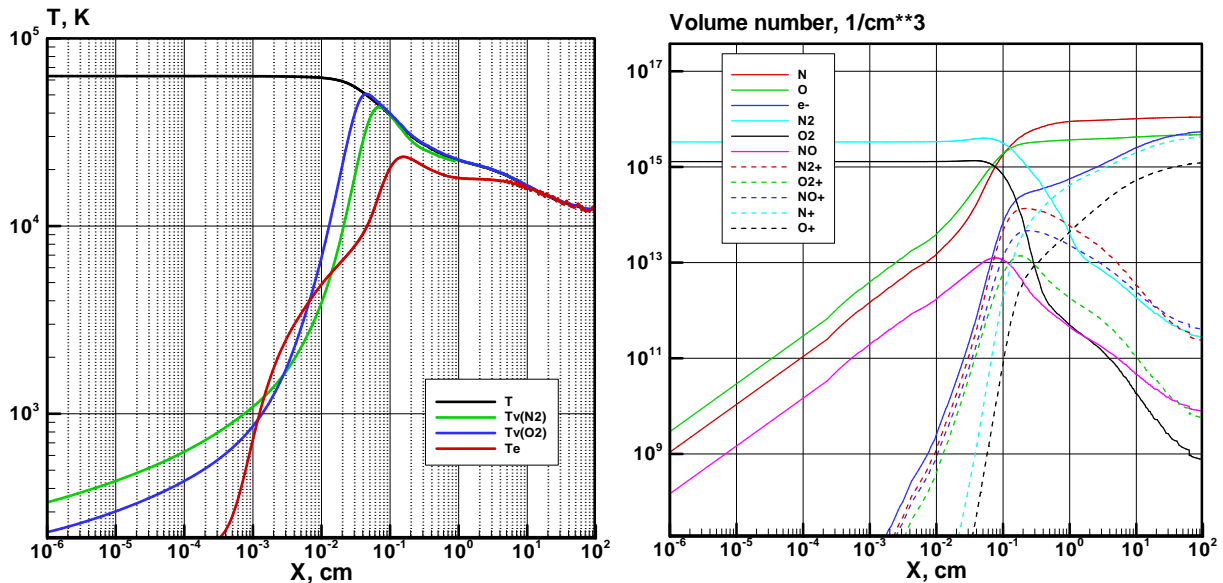
level;  $S_{v'v''}$  is the probability of the electronic-vibrational transition;  $E_{eel}(v')$  is the vibrational energy of the  $v'$ -th level of the excited electronic level;  $T_v, T_r = T$  are the vibrational and rotational temperatures. To calculate a spectral radiation flux the optically thin approximation was applied in the following form  $J_\lambda = 0.5 j_\lambda \delta$ , where  $\delta$  is the width of the emitting plane layer, which can be estimated for the experiments on shock waves emission as  $\delta = t_{em} U_s$  (here  $t_{em}$  is the duration of the radiation impulse behind the shock wave,  $U_s$  is the shock wave velocity).

Detailed study of the radiation model and description of the used initial data are presented in [31].

## 7.2 Numerical simulation results for air shock waves

Developed models of physical-chemical kinetics and non-equilibrium radiation were used for interpretation of Fire-II experimental data [86-88], and also of experimental data obtained at TsAGI shock tube ADST [69].

Numerical study of shock wave relaxation zone in air at five trajectory points of Fire-II flight experiment are presented in Figures 7.1–7.8.



**Figure 7.1: Shock wave relaxation zone in air at  $V_0 = 11.36$  km/s,  $p_0 = 20.8$  erg/cm<sup>3</sup>,  $T_0 = 195$  K (Fire-II, trajectory point  $t = 1634$  s); temperature distribution behind shock wave front (left), volume concentration (right);  $\alpha_q, \beta_q = 0.005$**

Figures 7.1 show respectively distributions of translation-rotational temperature ( $T$ ), vibrational temperatures ( $T_v(N_2)$ ,  $T_v(O_2)$ ), electron temperature ( $T_e$ ), and volume concentrations of chemical species. Figures 7.1–7.3 show numerical simulation data for the first trajectory point ( $t = 1634$  s) at three values of coefficients of energy transformation at associative ionization and dissociate recombination ( $\alpha_q, \beta_q$ ). It is clearly seen from these data that increasing of these coefficients leads to increasing of electronic temperature at distances  $\sim 10^{-3} \div 10^{-1}$  cm. This is very significant zone for non-equilibrium radiation generated by electronically excited states in diatomic molecules and free radicals.

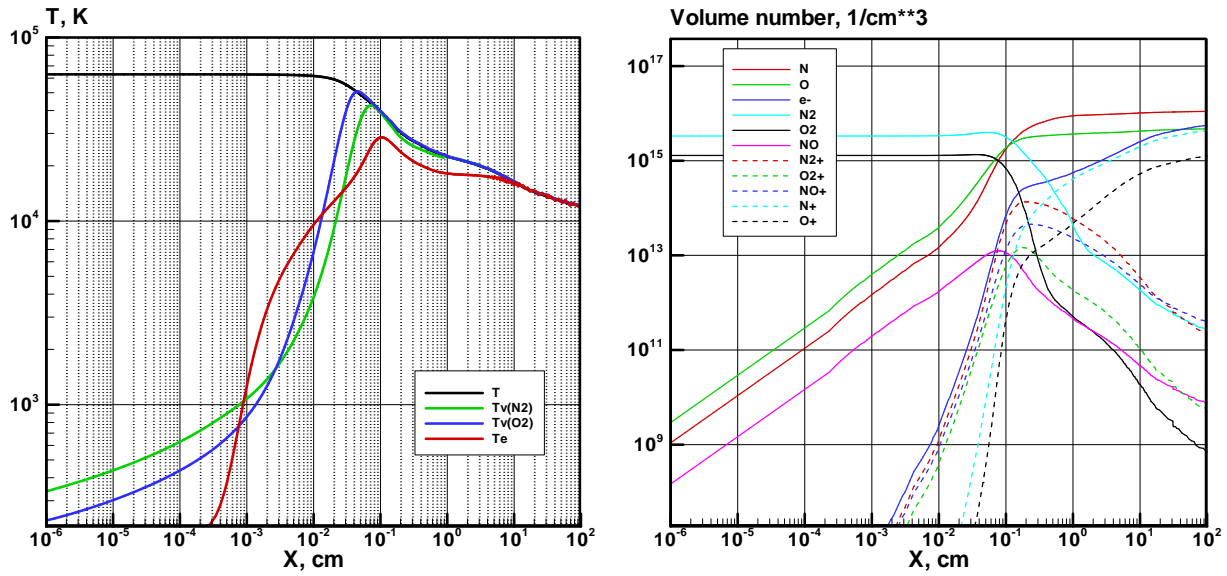


Figure 7.2: Shock wave relaxation zone in air at  $V_0 = 11.36$  km/s,  $p_0 = 20.8$  erg/cm<sup>3</sup>,  $T_0 = 195$  K (Fire-II,  $t = 1634$  s); temperature distribution behind shock wave front (left), volume concentration (right);  $\alpha_q, \beta_q = 0.01$

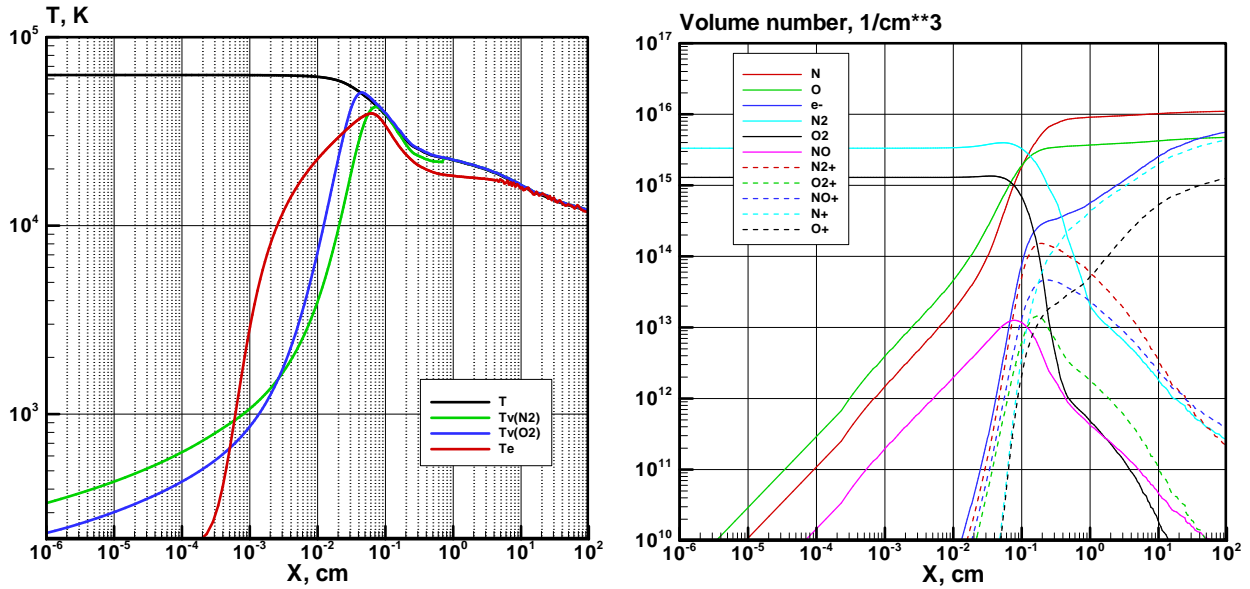


Figure 7.3: Shock wave relaxation zone in air at  $V_0 = 11.36$  km/s,  $p_0 = 20.8$  erg/cm<sup>3</sup>,  $T_0 = 195$  K (Fire-II,  $t = 1634$  s); temperature distribution behind shock wave front (left), volume concentration (right);  $\alpha_q, \beta_q = 0.05$

The influence of electronic temperature on non-equilibrium radiation of N<sub>2</sub>, O<sub>2</sub>, NO, N<sub>2</sub><sup>+</sup>, and O<sub>2</sub><sup>+</sup> is illustrated in Figures 7.4–7.5. Note, that overshoot of coefficients  $\alpha_q, \beta_q$  leads to significant overshoot of total radiation intensity. Presented data show that the most significant electronic bands in conditions under consideration are:  $b^1\Sigma_u^+ - X^1\Sigma_g^+$  (N<sub>2</sub>),  $C^2\Sigma_u^+ - X^2\Sigma_g^+$  (N<sub>2</sub><sup>+</sup>),  $D^3\Sigma_u^+ - B^3\Pi_g$  (N<sub>2</sub>),  $B^3\Sigma_u^- - X^3\Sigma_g^-$  (O<sub>2</sub>),  $C^3\Pi_u - B^3\Pi_g$  (N<sub>2</sub><sup>2</sup>),  $B^2\Sigma_u^+ - X^2\Sigma_g^+$  (N<sub>2</sub><sup>+</sup>),  $B^3\Pi_g - A^3\Sigma_u^+$  (N<sub>2</sub>),  $A^2\Pi_u - X^2\Sigma_g^+$  (N<sub>2</sub><sup>+</sup>).



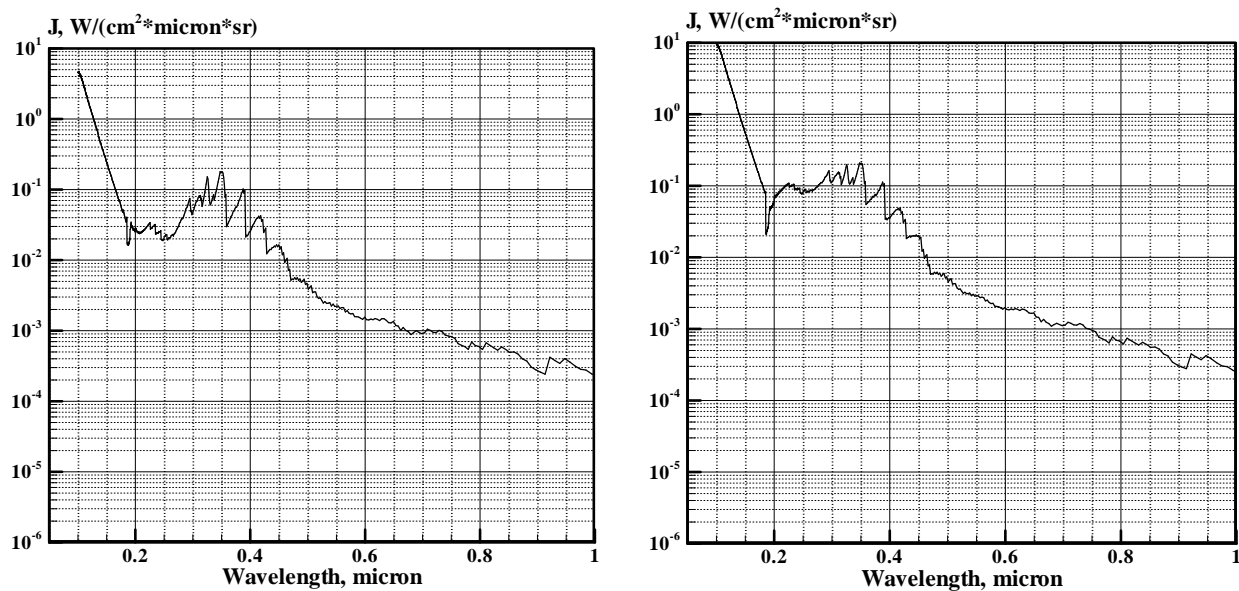


Figure 7.4: Total emissivity integrated by time at  $V_0 = 11.36$  km/s,  $p_0 = 20.8$  erg/cm<sup>3</sup>,  $T_0 = 195$  K (Fire-II,  $t = 1634$  s);  $\alpha_q, \beta_q = 0.05$  (left),  $\alpha_q, \beta_q = 0.01$  (right)

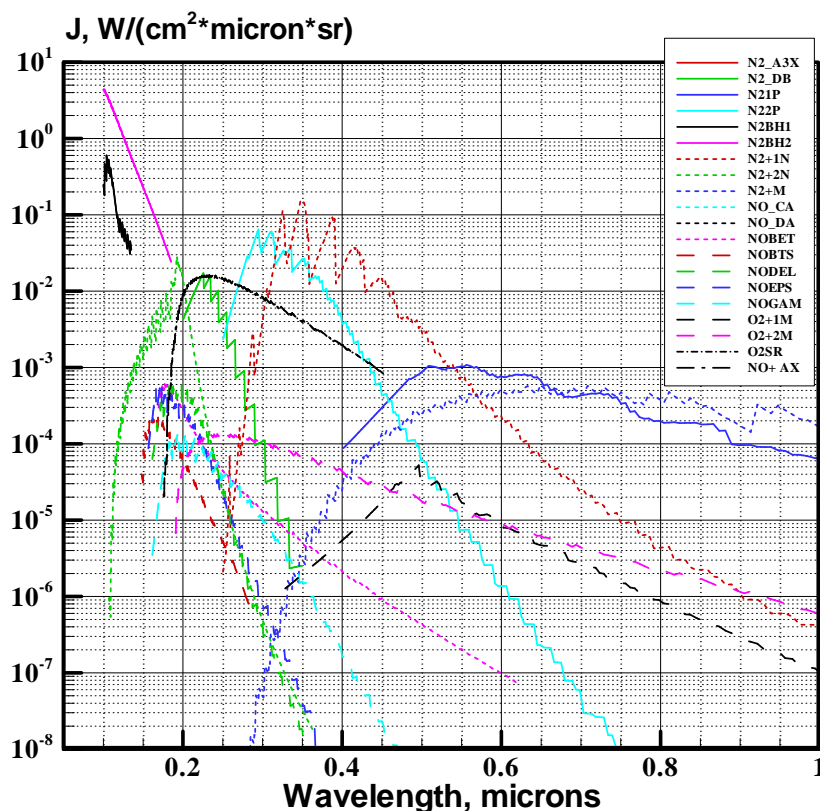


Figure 7.5: Partial spectral emissivity integrated by time at  $V_0 = 11.36$  km/s,  $p_0 = 20.8$  erg/cm<sup>3</sup>,  $T_0 = 195$  K (Fire-II,  $t = 1634$  s);  $\alpha_q, \beta_q = 0.05$

Figure 7.6 show that three most significant mechanisms determine electronic temperature in zone of strong non-equilibrium radiation. These are: associative ionization, heating at electron-vibrational interaction,

heating at collision ionization.

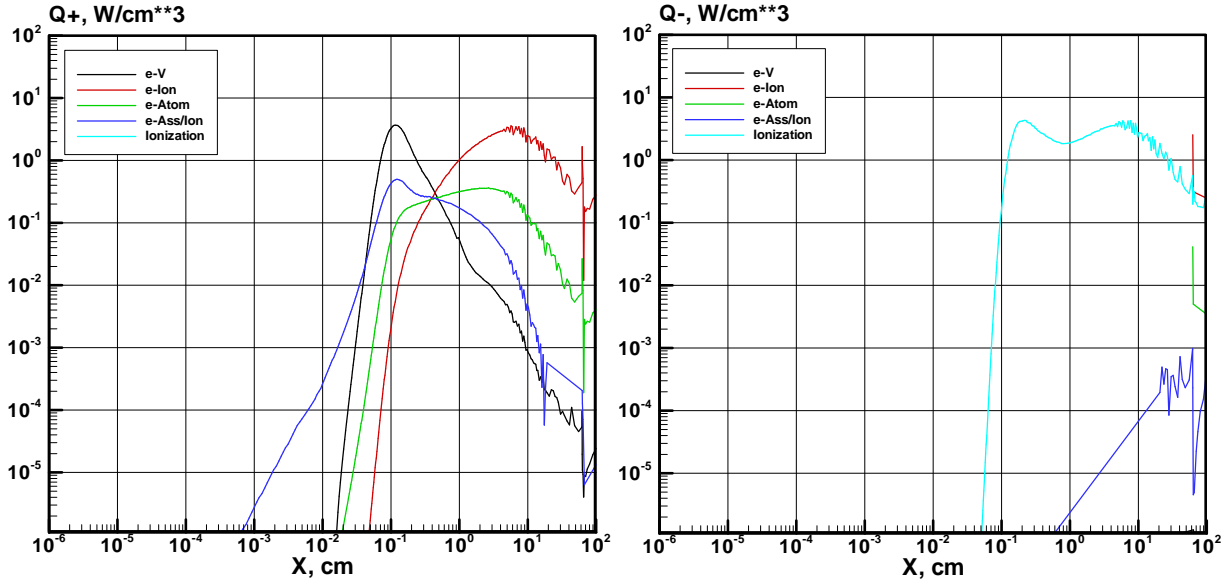


Figure 7.6: Shock wave relaxation zone in air at  $V_0 = 11.36$  km/s,  $p_0 = 20.8$  erg/cm<sup>3</sup>,  $T_0 = 195$  K (Fire-II,  $t = 1634$  s); sources of heating of electronic gas (left); sources of cooling of electronic gas (right).  $\alpha_q, \beta_q = 0.005$

Figure 7.7 demonstrates decreasing of relaxation zone behind shock wave in Fire-II experiment at successive trajectory points. It is seen that at increasing of time (that means decreasing of velocity and altitude of flight, see Table 7.2 in Ref. [86]) length of the relaxation zone decreases and electronic temperature rises sharply and approaches to translational temperature of heavy particles. Figures 7.8 and 7.9 illustrate this behaviour of spectral emissivity of shock wave integrated in time.

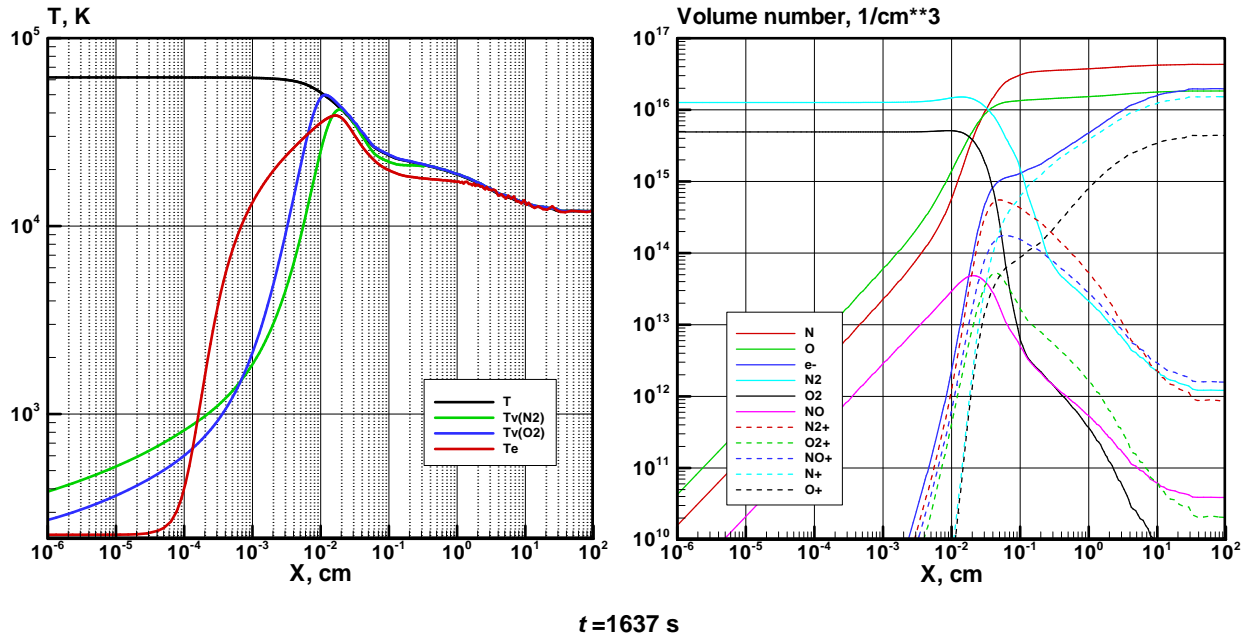


Figure 7.7: Temperature distribution and volume concentrations at successive trajectory points; Fire-II;  $\alpha_q, \beta_q = 0.01$  (beginning)

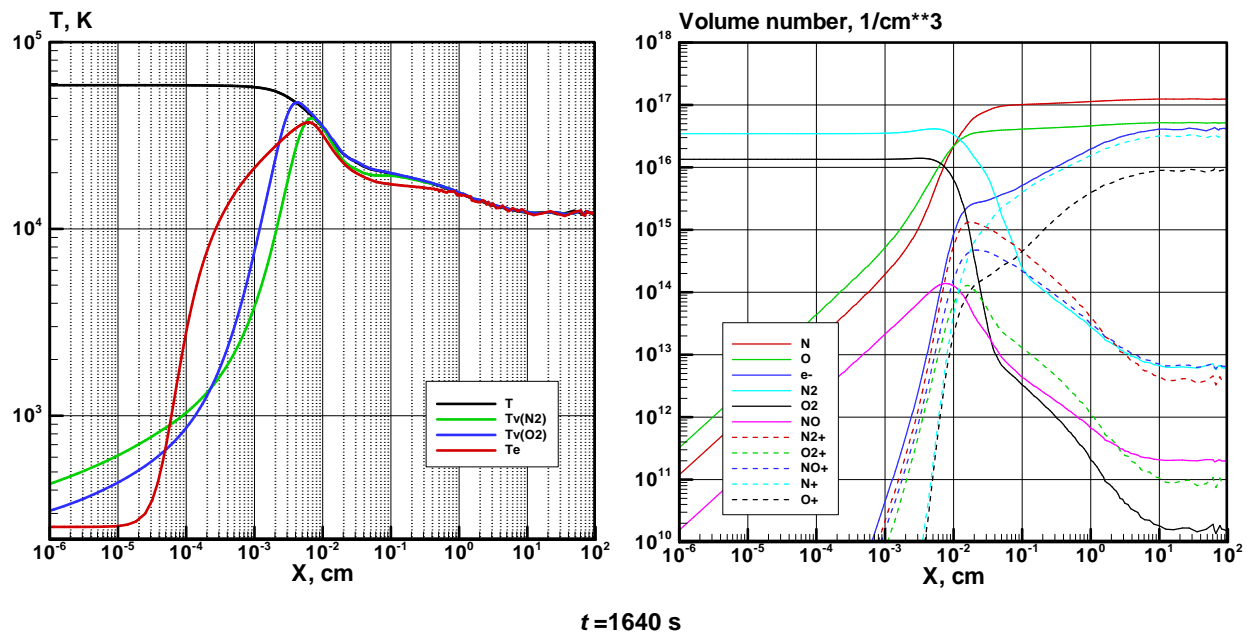


Figure 7.7: Temperature distribution and volume concentrations at successive trajectory points;  
Fire-II;  $\alpha_q, \beta_q = 0.01$  (continue)

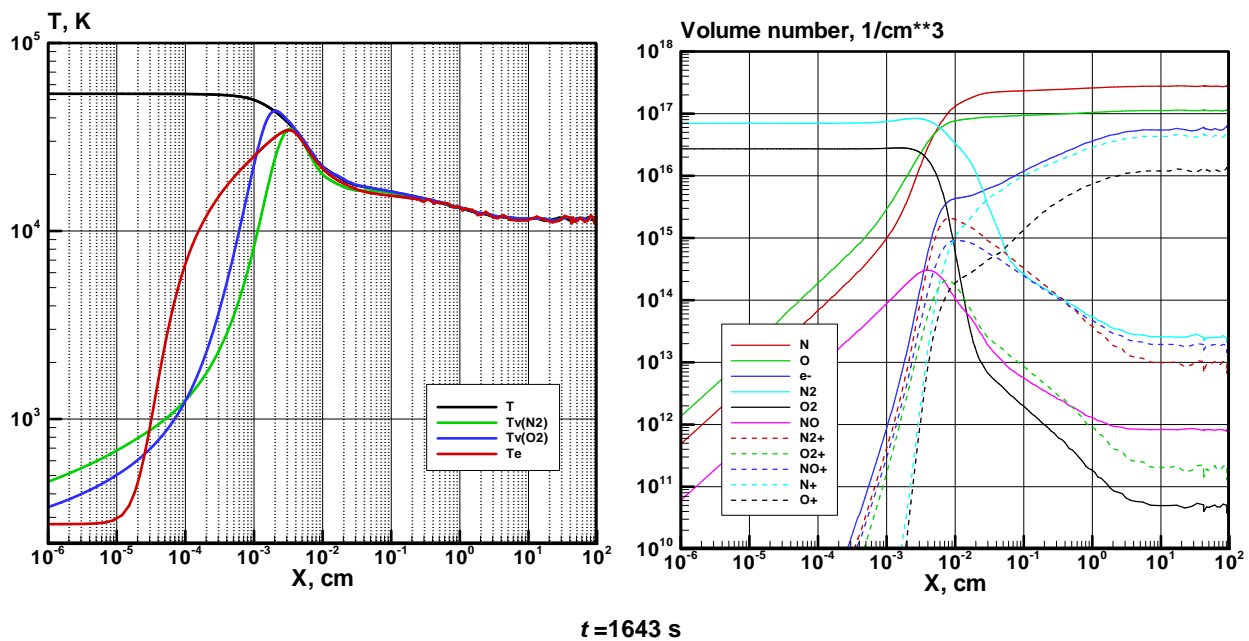


Figure 7.7: Temperature distribution and volume concentrations at successive trajectory points;  
Fire-II;  $\alpha_q, \beta_q = 0.01$  (continue)

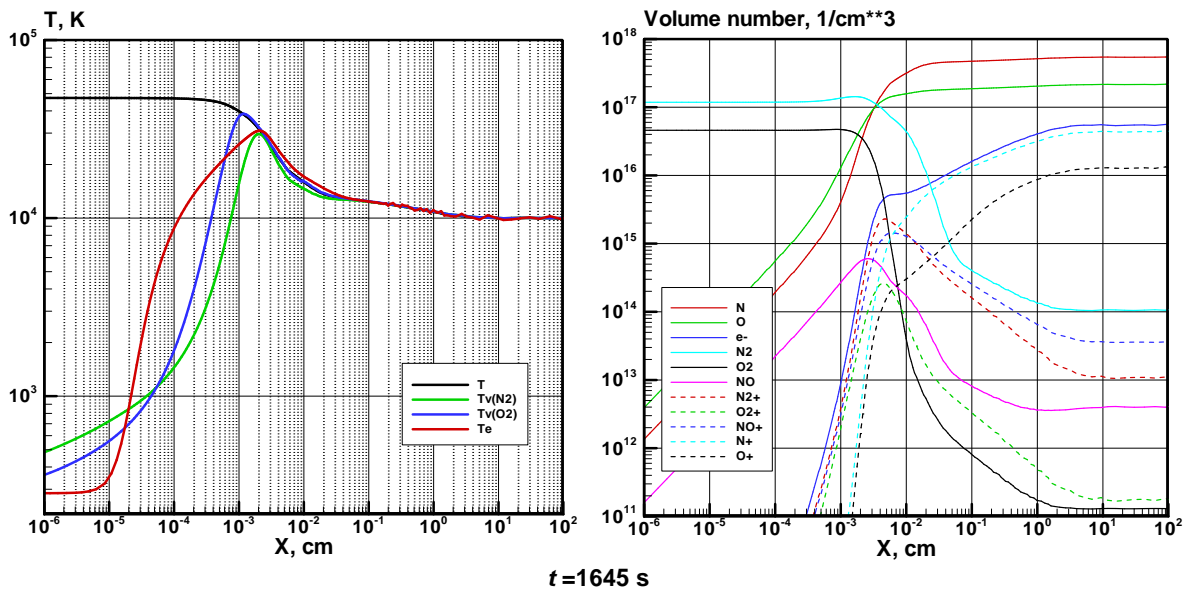


Figure 7.7: Temperature distribution and volume concentrations at successive trajectory points; Fire-II;  $\alpha_q, \beta_q = 0.01$

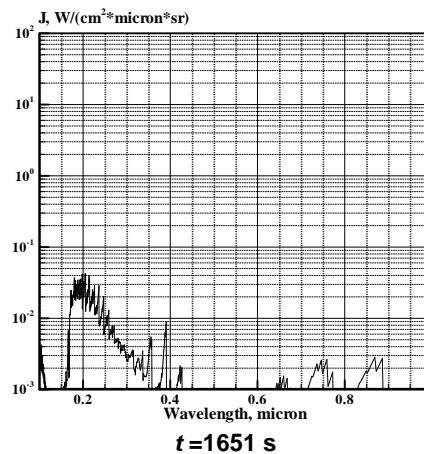
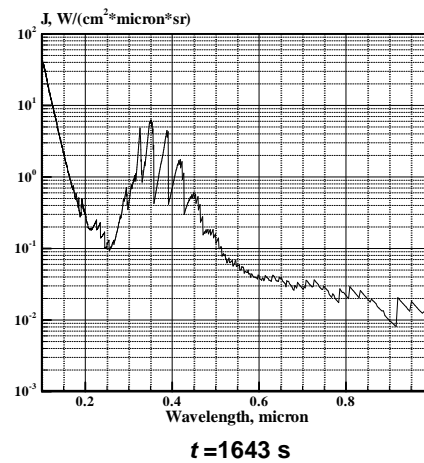
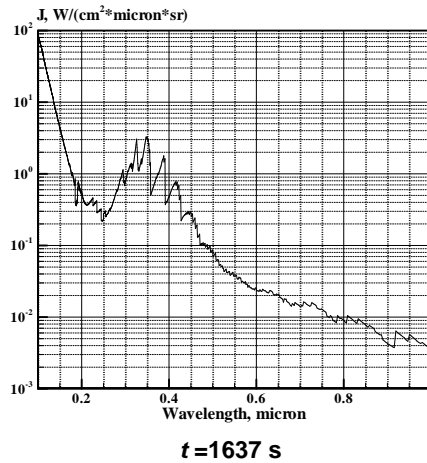


Figure 7.8: Total emissivity integrated by time at successive trajectory points (Fire-II);  $\alpha_q, \beta_q = 0.01$

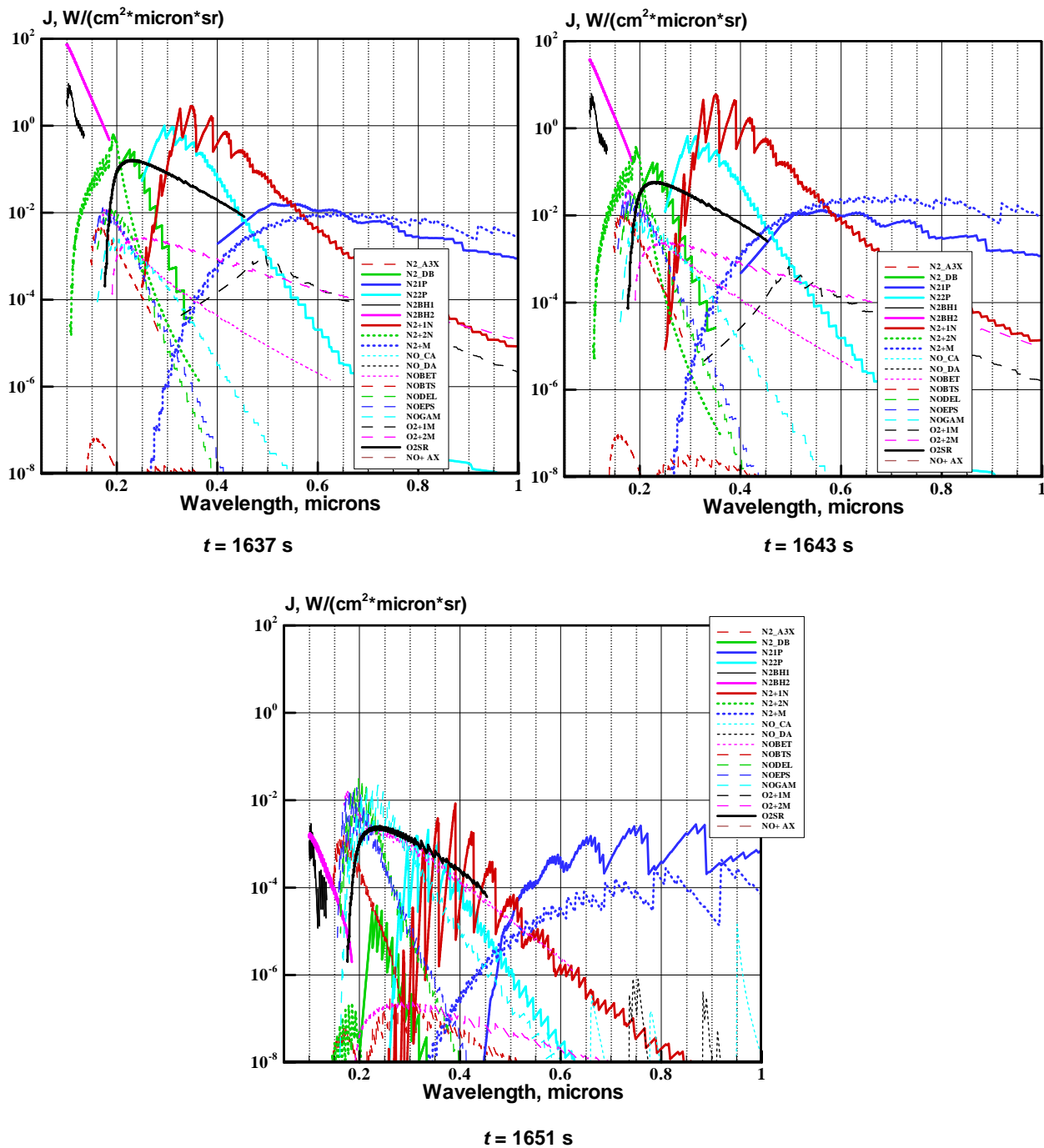
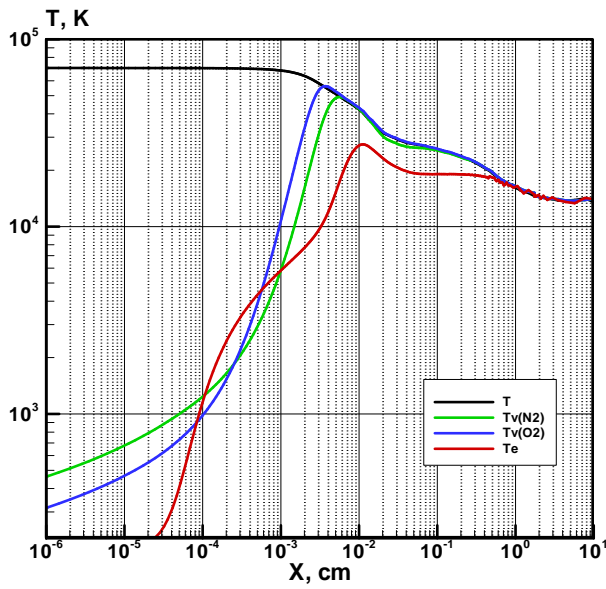
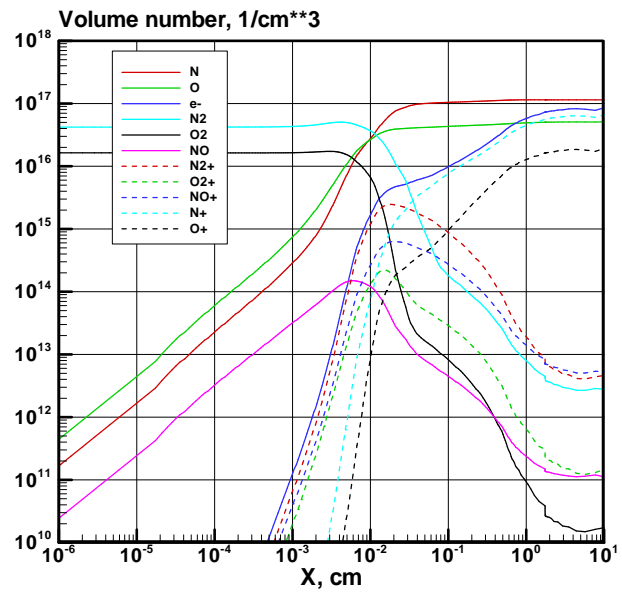


Figure 7.9: Partial spectral emissivity integrated by time at successive trajectory points (Fire-II);  $\alpha_q, \beta_q = 0.01$

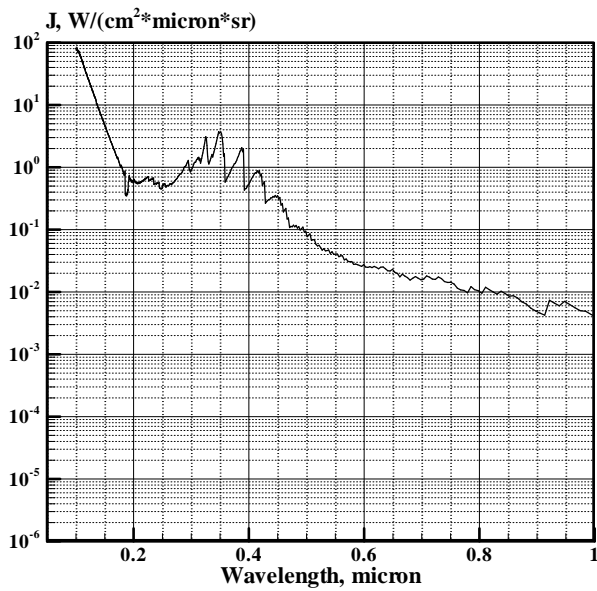
Developed numerical simulation model was used also for interpretation of experimental data obtained by V.Gorelov et al. [69]. Numerical simulation data presented in Figures 7.10 and 7.11 demonstrate some excess of numerical prediction of electronic concentrations of the experimental data.



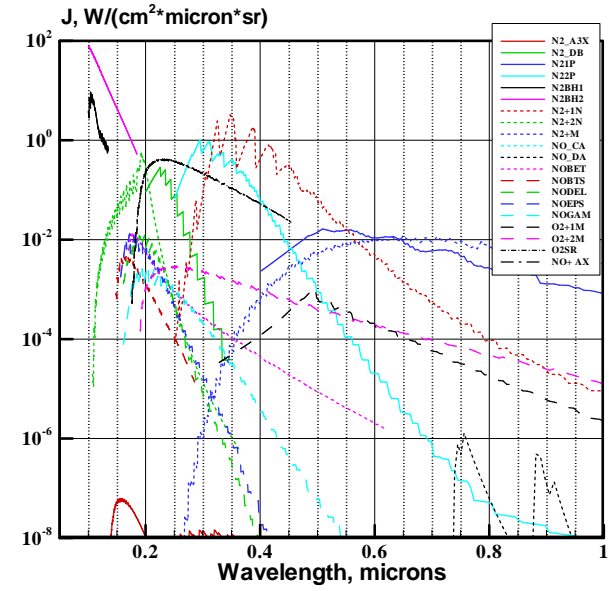
(a)



(b)



(c)



(d)

Figure 7.10: Shock wave relaxation zone in air at  $V_0 = 12$  km/s,  $p_0 = 263$  erg/cm<sup>3</sup> (experiments [69]): temperature distribution behind shock wave front (a), volume concentration (b); total (c) and partial spectral emissivity (d) integrated by time;  $\alpha_q, \beta_q = 0.05$



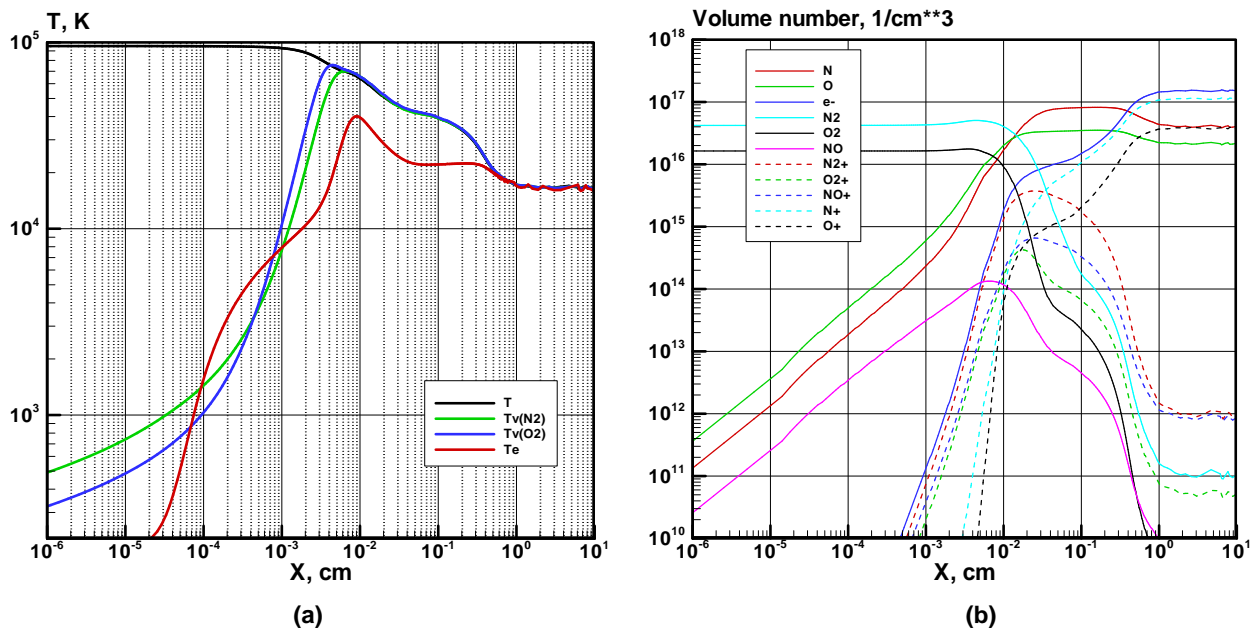


Figure 7.11: Shock wave relaxation zone in air at  $V_0 = 14$  km/s,  $p_0 = 263$  erg/cm<sup>3</sup> (experiments [69]): temperature distribution behind shock wave front (a), volume concentration (b);  $\alpha_q, \beta_q = 0.05$

### 7.3 Numerical simulation results for CO<sub>2</sub>–N<sub>2</sub>–Ar mixtures

The following three calculation series were performed for such mixtures:

- Prediction of the non-equilibrium radiation for the Thomas and Menard [73] experimental measurements;
- Radiation spectra calculations for the stagnation point conditions studied by Park, Howe, Jaffe and Candler [3];
- Calculations of the non-equilibrium radiation of mixtures CO<sub>2</sub>–N<sub>2</sub>–Ar in shock waves for the P. Kozlov, S. Losev and Yu. Romanenko [89] experimental measurements.

#### 7.3.1 Comparison with the Thomas – Menard experimental data

Calculation data were obtained for the following three mixtures studied by Thomas and Menard [73]: 9%CO<sub>2</sub>–90%N<sub>2</sub>–1%Ar (Figures 7.12), 30%CO<sub>2</sub>–70%N<sub>2</sub> (Figures 7.13). The following three molecular bands were analyzed in these calculations: CN Violet system ( $B^2\Sigma^+ - X^2\Sigma^+$ ), CN Red system ( $A^2\Pi - X^2\Sigma^+$ ), and C<sub>2</sub> Swan system ( $d^3\Pi_g - a^3\Pi_u$ ). Figures 7.12 show spectral distribution of the non-equilibrium radiation behind the shock waves for the gas mixture 9%CO<sub>2</sub>–90%N<sub>2</sub>–1%Ar at  $p_0 = 0.25$  torr and  $U_s = 7620$  m/s. In the first case (left figure) the Boltzmann distribution of excited electronic levels was presumed, that is the populations of the excited levels were determined by translational temperature of the heavy particles. In the second case the radiative-collisional model for excited electronic levels was used. Comparison of the calculations with the experimental data [73] is also presented in Figures 7.12.

Distributions of the volume concentrations and also translational, vibrational (for different vibrational modes) and electronic temperatures are presented in Figures 7.13 for the second mixture (30%CO<sub>2</sub>–70%N<sub>2</sub>). In this case a most intensive radiation was observed in the experiments. The present calculations are in good accordance with the regularity. Figure 7.13,b shows spectral distribution of corresponding non-equilibrium radiation intensity for the radiative-collisional model of excited electronic levels of diatomic molecules.

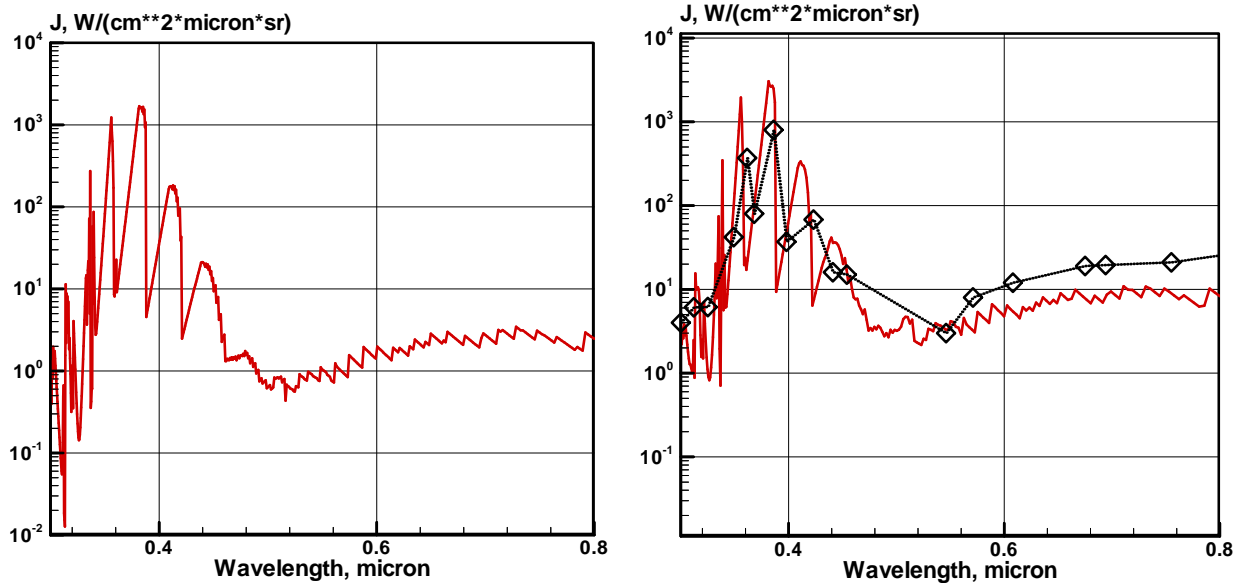


Figure 7.12: Non-equilibrium radiation behind the shock wave for the Thomas-Menard experiments [73]:  $p_0 = 0.25$  torr and  $U_s = 7620$  m/s (9%CO<sub>2</sub>–90%N<sub>2</sub>–1%Ar). The Boltzmann distribution of excited electronic levels (left), and the radiative-collisional model for excited electronic levels (right). Calculations (solid line) and experimental data [73] (diamonds)

As seen from the data presented, the present calculations allow to get satisfactory description of the experimental data. But, at the same time, one can find also significant differences in some ranges of the spectra. Numerical experiments showed that it is possible to achieve better fit of the experimental data by variation of used kinetic constants (but corresponding problem demands a separate detailed discussion).

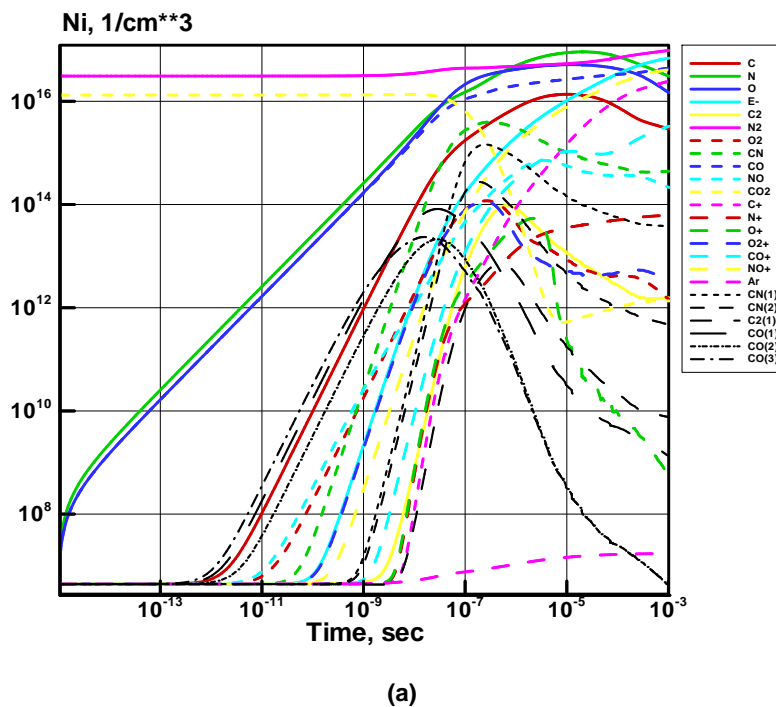
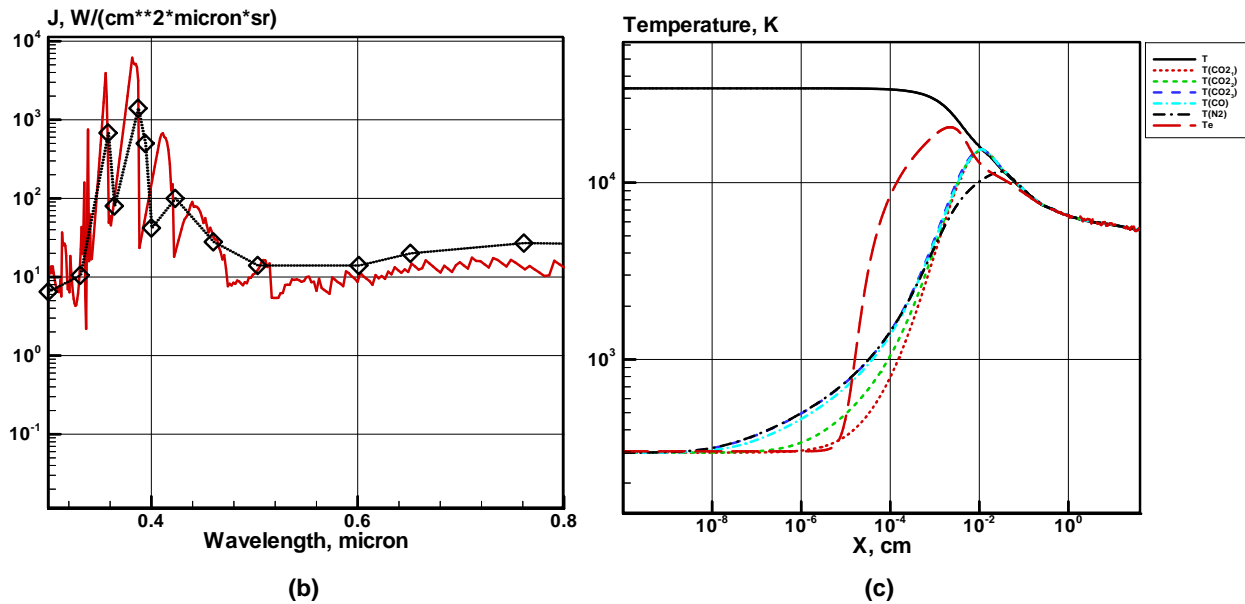


Figure 7.13: (beginning)





**Figure 7.13: Temporary behaviour of species volume concentrations (a) and temperatures (b) behind the shock wave for the Thomas – Menard experiments [73]:  $p_0 = 0.25$  torr and  $U_s = 7620$  m/s (30%CO<sub>2</sub>–70%N<sub>2</sub>). The radiative-collisional model for excited electronic levels is presumed. Non-equilibrium radiation behind the shock wave (b). Calculations (solid line) and experimental data [73] (diamonds)**

### 7.3.2 Comparison with the Park – Howe – Jaffe – Candler calculated data

Calculation data were obtained for the following gas mixture studied in [3]: 95.7%CO<sub>2</sub>–2.7%N<sub>2</sub>–1.6%Ar (Figures 7.14). The calculations were performed for the initial pressure  $p_0 = 0.133$  torr. This pressure provides pressure  $p = 0.15$  atm behind the shock wave with velocity  $U_s = 8000$  m/s (just these conditions have been studied in [3]). In this case the following four molecular bands were taken into account: CN Violet system ( $B^2\Sigma^+ - X^2\Sigma^+$ ), CN Red system ( $A^2\Pi - X^2\Sigma^+$ ), C<sub>2</sub> Swan system ( $d^3\Pi_g - a^3\Pi_u$ ), and also CO 4<sup>th</sup> positive system ( $A^1\Pi - X^1\Sigma^+$ ).

Numerical experiments were performed as previously for the two models of excitation of the diatomic molecules electronic levels. Spectral distribution of the non-equilibrium radiation for the Boltzmann model and for the radiative-collisional model are shown in Figure 7.14 (see also Figs.7.15,7.16). It should be noted that comparison of these data for the local thermodynamic equilibrium conditions was previously performed to define more accurately corresponding kinetic constants. One can see that for conditions under consideration differences between spectral intensities significant enough, especially for the CO 4<sup>th</sup> positive system ( $0.15 < \lambda < 0.2 \mu\text{m}$ ), the CN Red system ( $0.6 < \lambda < 0.8 \mu\text{m}$ ) and the C<sub>2</sub> Swan system ( $0.4 < \lambda < 0.55 \mu\text{m}$ ).

### 7.3.3 Comparison with the Kozlov – Losev – Romanenko experimental data

Calculation data were obtained for the following two mixtures studied in [89]: 9.6%CO<sub>2</sub>–0.3%N<sub>2</sub>–90.1%Ar, and 4.8%CO<sub>2</sub>–0.15%N<sub>2</sub>–95.05%Ar. Figures 7.17 show spectral distribution of the non-equilibrium radiation behind shock wave fronts for the first mixture at  $p_0 = 1.0$  torr and  $U_s = 3450$  m/s. The Boltzmann distribution of excited electronic levels and radiative-collisional model were presumed for calculations presented in this figures. Time behavior of the volume concentrations and corresponding spatial distribution of the temperatures are shown in Figures 7.18. Analogous data for the second mixture are presented in Figures 7.19.

All calculated data presented above were obtained using kinetic constants for the radiative-collisional model recommended in Ref. [79]. Another set of the constants suggested early by Dravin and Emard [90] and by Zalagin et al. in [91] (see Tables RD.12) were also used. Calculation data obtained with these kinetic constants are shown in Figures 7.20. Comparison of these presented data allows make a conclusion concerning effect of the constants on the system of studied kinetic processes.

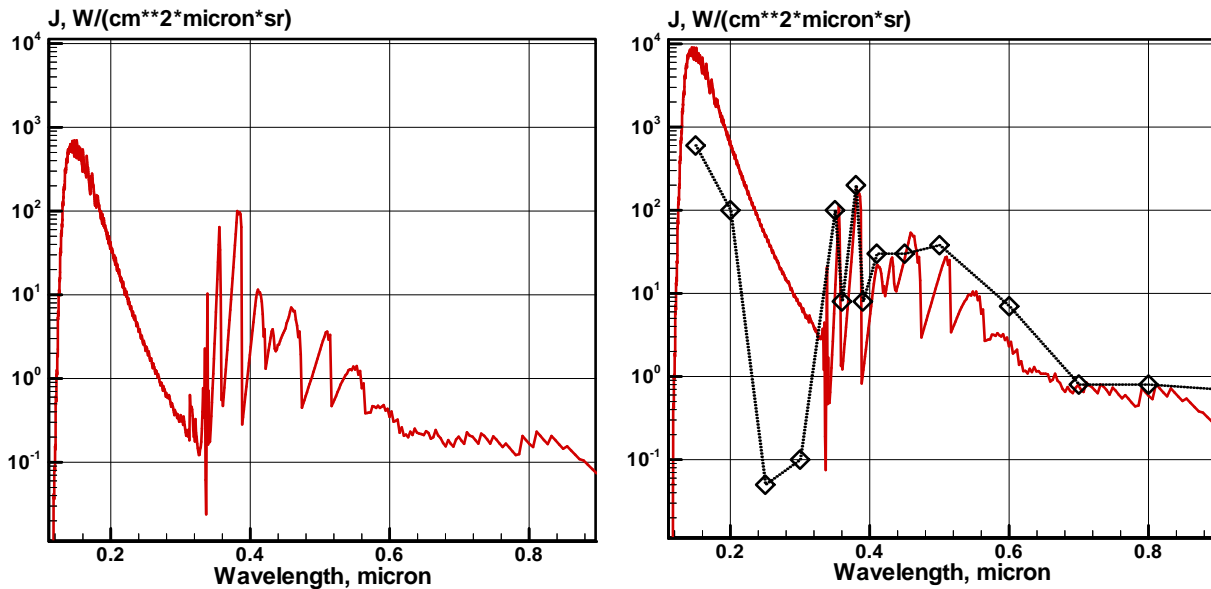


Figure 7.14: Non-equilibrium radiation behind the shock wave for conditions of the Park-Howe-Jaffe-Candler calculations [3]:  $p_0 = 0.133$  torr and  $U_s = 8000$  m/s (95.7%CO<sub>2</sub>–2.7%N<sub>2</sub>–1.6%Ar). The Boltzmann distribution of excited electronic levels (left), and the radiative-collisional model for excited electronic levels (right): present calculations (solid line) and some calculated points [3] (diamonds)

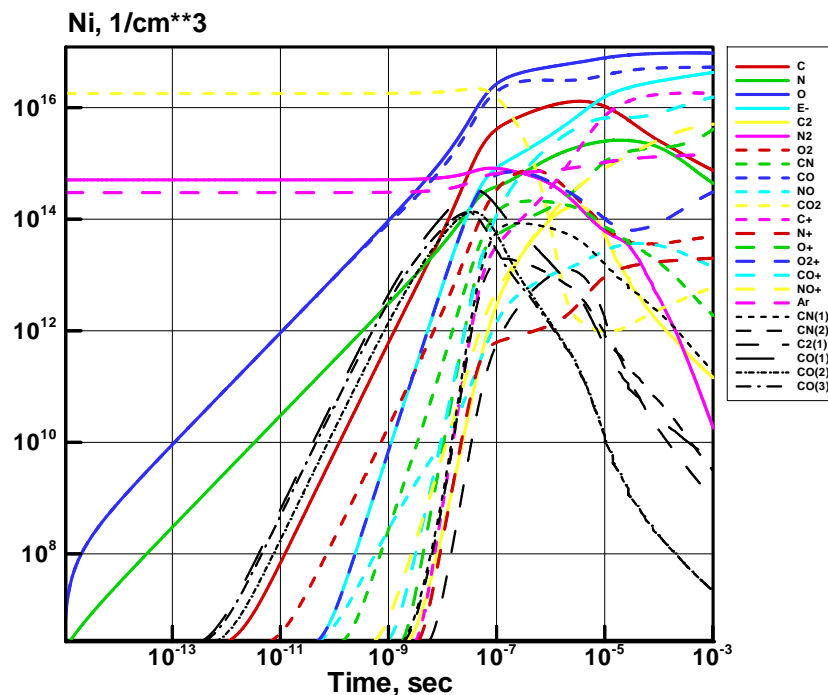


Figure 7.15: Temporary behavior of species volume concentrations behind the shock wave for conditions of the Park-Howe-Jaffe-Candler calculations [3]:  $p_0 = 0.133$  torr and  $U_s = 8000$  m/s (95.7% CO<sub>2</sub>–2.7%N<sub>2</sub>–1.6%Ar). The radiative-collisional model for excited electronic levels is presumed

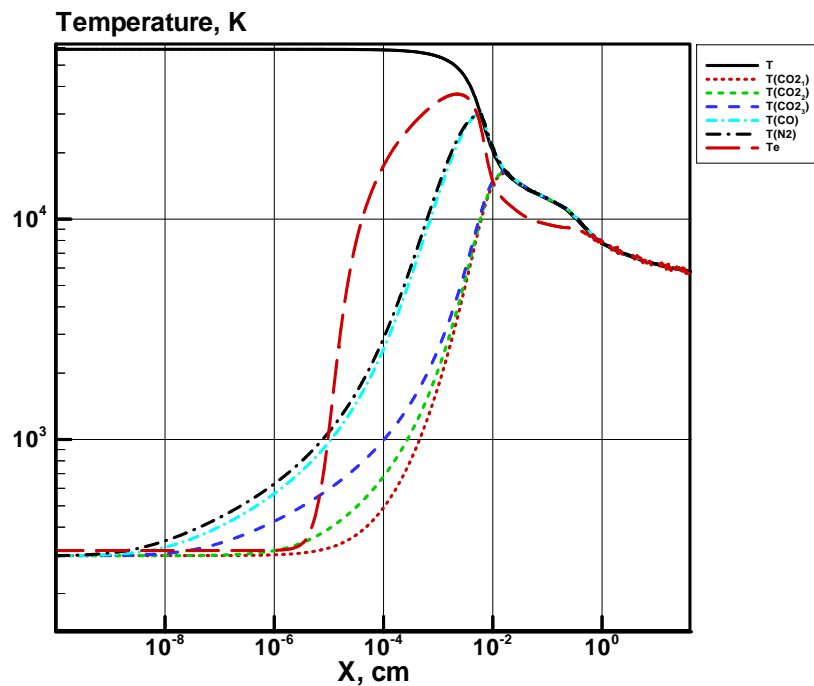


Figure 7.16: Temperature distributions behind the shock wave for conditions of the Park-Howe-Jaffe-Candler calculations [3]:  $p_0 = 0.133$  torr and  $U_s = 8000$  m/s (95.7%CO<sub>2</sub>-2.7%N<sub>2</sub>-1.6%Ar). The radiative-collisional model for excited electronic levels is presumed

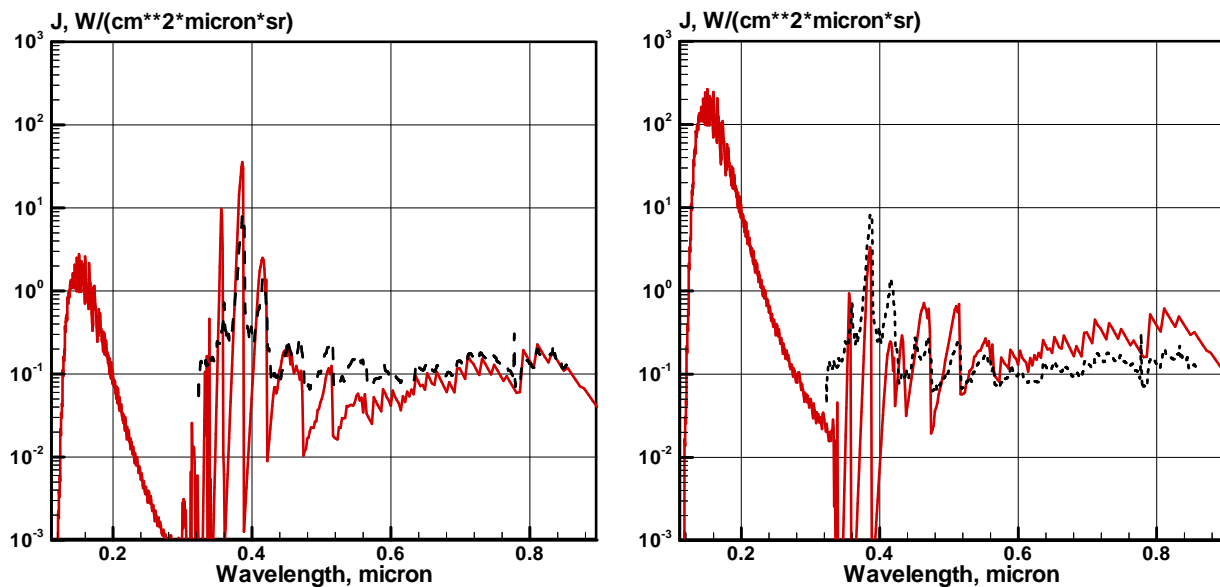


Figure 7.17: Non-equilibrium radiation behind the shock wave for conditions of the Kozlov-Losev-Romanenko experiments [20,23]:  $p_0 = 1.0$  torr and  $U_s = 3450$  m/s (9.6%CO<sub>2</sub>-0.3%N<sub>2</sub>-90.1%Ar). The Boltzmann distribution of excited electronic levels (left), and the radiative-collisional model for excited electronic levels (right): present calculations (solid line) and experimental data [89] (dotted line)

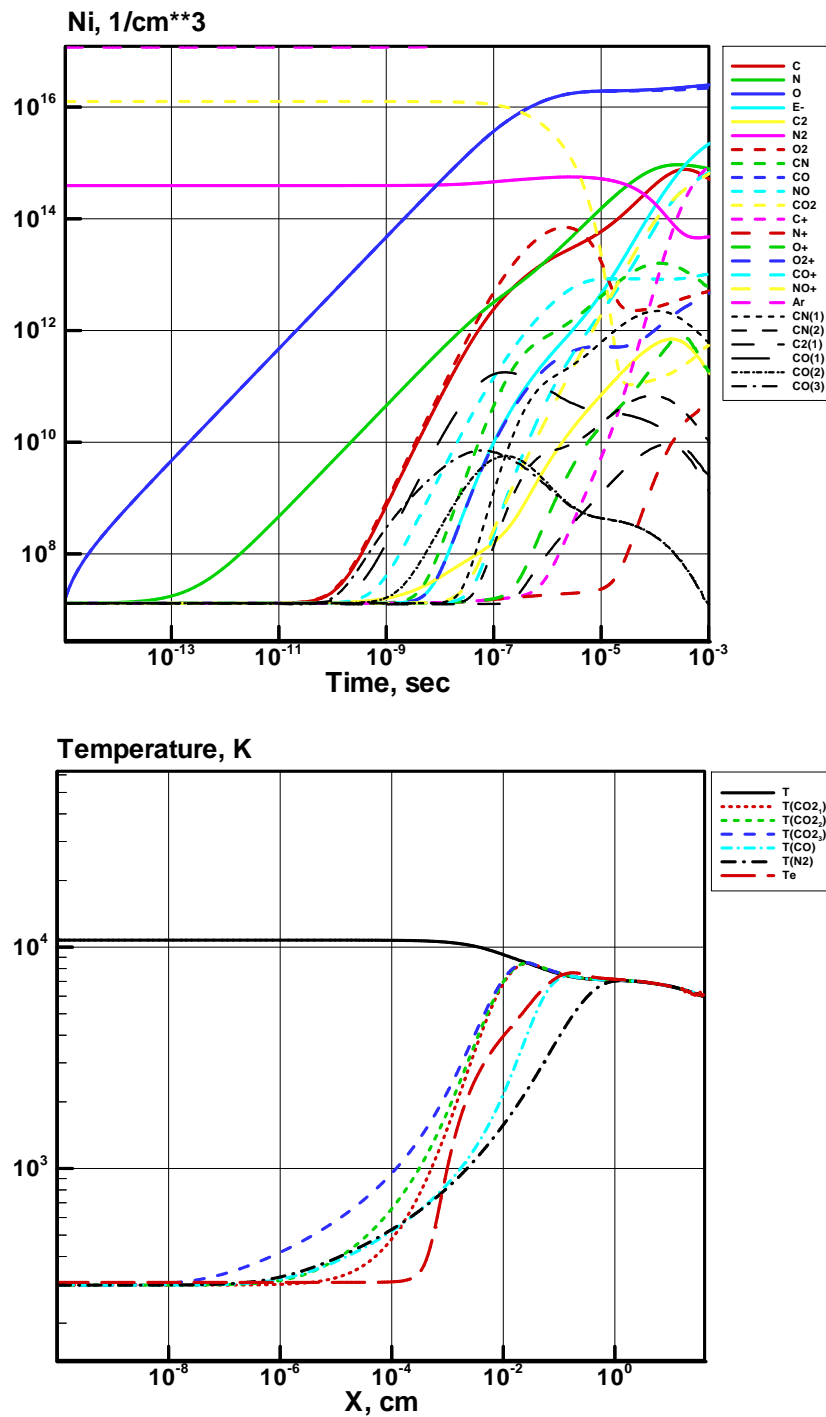


Figure 7.18: Temporary behavior of species volume concentrations and temperatures behind the shock wave for conditions of the Kozlov-Losev-Romanenko experiments [89]:  $\rho_0 = 1.0$  torr and  $U_s = 3450$  m/s (9.6%CO<sub>2</sub>–0.3%N<sub>2</sub>–90.1%Ar). The Radiative-collisional model for excited electronic levels is presumed

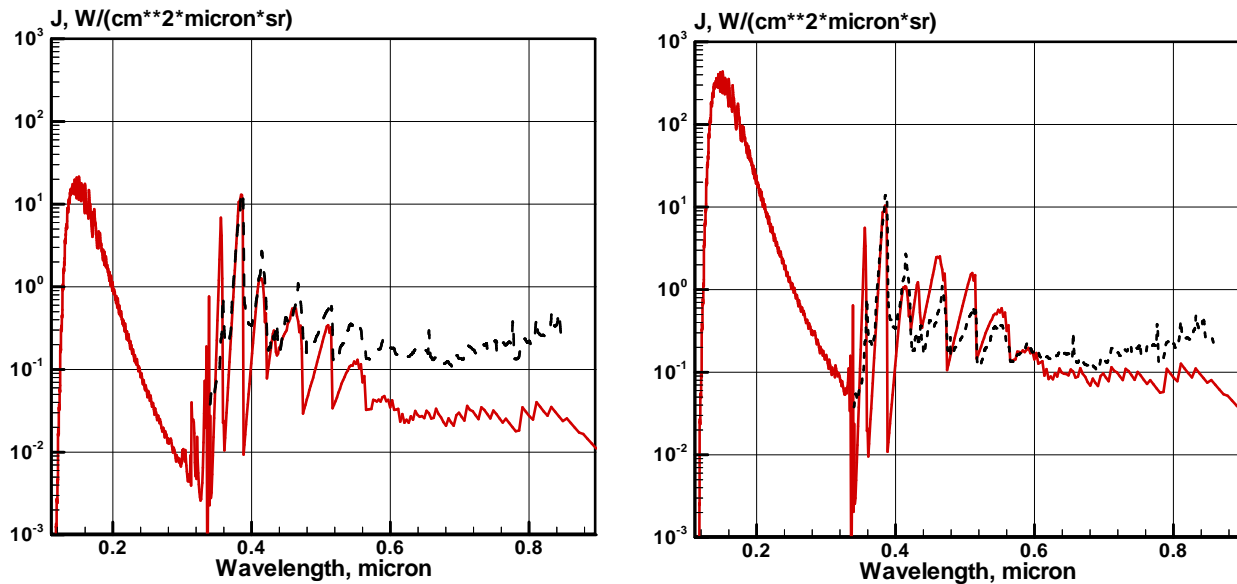


Figure 7.19: Non-equilibrium radiation behind the shock wave for conditions of the Kozlov-Losev-Romanenko experiments [89]:  $p_0 = 0.5$  torr and  $U_s = 3750$  m/s (4.8%CO<sub>2</sub>-0.15%N<sub>2</sub>-95.05%Ar). The Boltzmann distribution of excited electronic levels (left), and the radiative-collisional model for excited electronic levels (right). Present calculations (solid line) and experimental data [89] (dotted line)

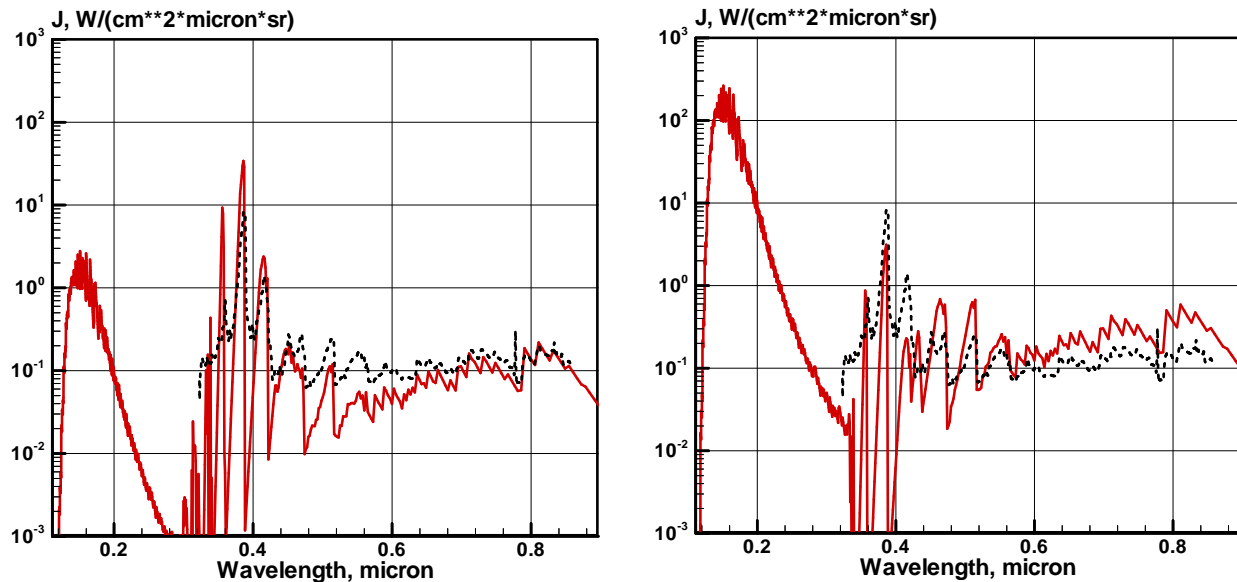


Figure 7.20: Non-equilibrium radiation behind the shock wave for conditions of the Kozlov-Losev-Romanenko experiments [89]:  $p_0 = 0.5$  torr and  $U_s = 3750$  m/s (4.8%CO<sub>2</sub>-0.15%N<sub>2</sub>-95.05%Ar). The Boltzmann distribution of excited electronic levels (left). The radiative-collisional model for excited electronic levels (right). Present calculations (solid line; the second set of constants of diatomic molecules electronic levels excitation) are compared with experimental data [89] (dotted line)

#### 7.4 Model of electronic kinetics of high-temperature air behind shock wave, tested in experiments [92]

This model contains kinetic description of the following processes:

- Vibrational relaxation;
- Coupled dissociation-vibrational excitation processes;
- Formation of NO molecules through the two-channel processes, including vibrational excited N<sub>2</sub>;
- Associative ionization;
- Ionization by an electronic impact;
- Vibrational relaxation due to electron-molecular collisions;
- Charge-exchange chemical processes.

The vibrational relaxation was considered in the frame of the model [25]. The relaxation time of species N<sub>2</sub>, O<sub>2</sub> at V-T processes calculated as follows:

$$p\tau = AT^n \exp\left(\frac{B}{T^{1/3}}\right),$$

where coefficients  $A, n, B$  are presented in Table RD11 (Appendix).

Vibrational relaxation of the NO molecules was calculated using Park model [2].

Vibrational excitation of N<sub>2</sub> by electronic impact was calculated with the Shultz model of step-by-step excitation [93].

Vibrational-dissociative coupling was taken into account by the  $\beta$ -model:

$$\Phi(T, T_v) = \frac{1 - e^{-(\theta/T_v)}}{1 - e^{-(\theta/T)}} \exp\left[-(D - \beta T)\left(\frac{1}{T_v} - \frac{1}{T}\right)\right],$$

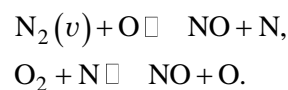
where  $D_{O_2} = 59400$  K,  $\beta_{O_2} = 1.5$  ;

$D_{N_2} = 113200$  K,  $\beta_{N_2} = 3.0$  ;

$D_{NO} = 75500$  K,  $\beta_{NO} = 3.0$  ;

Other constants are presented in Table RD11.

As it was mentioned above, formation of NO was considered in the frame of the following kinetic scheme:



For the first reaction the rate constant

$$k(T, T_{N_2, v}) = \frac{6.8 \times 10^{13}}{Q(T_{N_2, v})} \sum_v \exp \left[ \left( \frac{E_a}{T} - \frac{E_v}{T_{N_2, v}} \right) - \frac{E_a - \gamma E_v}{\beta T} \Theta(E_a - \gamma E_v) \right],$$

where  $E_a = 38000$  K,  $\beta = 0.9$ ;

$$Q(T_{N_2, v}) = \exp \left( -\frac{D}{T_{N_2, v}} \right) \frac{2}{1 - e^{-(\theta/T_{N_2, v})}};$$

$\Theta$  is the Heavisid function;  $E_v$  is the vibrational energy of  $N_2$ ;  $D$  is the dissociation energy of  $N_2$ .

For the second reaction [94].

$$k_f = 6.4 \times 10^9 T \exp \left( -\frac{3150}{T} \right), \frac{\text{cm}^3}{\text{mol} \cdot \text{s}}$$

Rate constants for electronic impact ionization are presented in Table RD11.

Kinetic processes with electrons are considered in the model in the frame of assumption about different temperatures of the electrons and heavy particles. The temperature of electrons  $T_e$  is calculated from the following electronic energy conservation equation:

$$\frac{d}{dx} \left( \frac{3}{2} T_e n_e \right) = Q_{ai} - Q_{el} - Q_{eR} - Q_{eV}, \quad (31)$$

where  $n_e$  is the concentration of electrons;  $Q_{ai}$  is the associative ionization energy exchange;  $Q_{el}$  is the energy exchange in elastic collisions between the electron and heavy particle;  $Q_{eR}$  is the energy exchange with rotational degrees of freedom of molecules;  $Q_{eV}$  is the energy exchange at interaction of the electrons with vibrational states of molecules  $N_2$  in the following reaction:



Enumerated terms in the right hand side of Equation (32) are formulated as follows:

$$Q_{ai} = \frac{3}{2} \sum_j (T R_{ffj} - T_e R_{rj}),$$

$$Q_{el} = \sum_i \frac{3m_e}{m_i} v_{ei} n_e (T - T_e),$$

$$Q_{eR} = \sum_m \frac{64}{\sqrt{3}} B_m \sqrt{\frac{8kT_e}{\pi m_e}} \sigma_R \left( \frac{T}{T_e} - 1 \right) n_m n_e,$$

$$Q_{eV} = \frac{n_e n_{N_2}}{q} \sum_v v \theta_{N_2} \left[ e^{-(v \theta_{N_2} / T_e)} \cdot \sum_{v'} k_{vv'}(T_e) e^{v' \theta_{N_2} (T_{N_2, v} - T_e)} - e^{-(v \theta_{N_2} / T_{N_2, v})} \cdot \sum_{v'} k_{vv'}(T_e) \right],$$

where  $R_{ff}, R_{rj}$  are the forward and reverse rates of association ionization reaction  $j$ ;  $m$  is the index of heavy particle ( $N_2$ ,  $O_2$ ,  $NO$ );  $B_m$  is the rotational constant of the molecule species  $m$ ;  $\sigma_R$  is the cross section of electronic-rotation interaction:

$$\sigma_R = \frac{2\pi}{15} \frac{s_m^2}{ea_0^2},$$

where  $s_m$  is the molecular quadrupole moment;  $q$  is the vibrational  $N_2$  partition function;  $k_{vv'}(T_e)$  is the rate constant for reaction (32) (see Table RD11).

Reactions of charge exchange between ions of atoms and molecules with corresponding rate constants are presented in Table RD11. Electronic kinetics in the model [92] is also presented by the reactions which are determined radiation emissivity of  $NO$ ,  $N_2$ ,  $N_2^+$ . Rate constants of these reactions are presented in Tables RD11.

It should be taken into account that authors of [92] assume that electronic temperature at shock wave fronts coincides with translational temperature of heavy particles. This assumption differs from that in the model presented in Section 7.1.

## 7.5 Models of electronic kinetics for super-orbital entry velocities [95-98]

Several models of electronic kinetics were suggested and studies in series of publications of L. Carlson and his assistants, and his scientific assistances [95-98]. Electron-impact ionization rates in nitrogen and oxygen were discussed in [96]. It was shown that exciting rates of electronic kinetics in the literature varied over several orders of magnitude with accompanying differences in profiles of electronic temperature  $T_e$  and wall radiative heating rates, which is a strong function of  $T_e$ . Analogues results were recently demonstrated in [75].

The effects of thermodynamic Nonequilibrium on the magnitude and nature of the radiative heat transfer processes were studied in [97]. Comparison was performed with flight experiment FIRE-II, and a wide range of possible space missions profile conditions were studies.

Significant coupled effects of dissociation and vibrational relaxation were considered in [98].

Authors of [95] discussed in details a two-step excitation model for atomic nitrogen. The model assumes that the excitation jump from ground to the first excited state controls the ionization processes, and that the excited states are in equilibrium with free electrons and ions, because of their proximity in energy to the ionized state. Note, that models of Park [99] and Kunc and Soon [100] handle possible local thermodynamic Nonequilibrium (LTNE) effects by performing detailed state population calculations under the quasisteady (QSS) assumptions. These methods are computationally intensive, and, therefore, these are not very suitable for radiative-gasdynamic coupling.

Authors of [96] suggested so called a second-order LTNE model for high-temperature nitrogen by subdividing atomic nitrogen into two species. The first, termed  $N_g$ , for N ground, represents the nitrogen atoms in the first three low-lying electronic states of nitrogen ( $E = 19223, 19231, 28840 \text{ cm}^{-1}$ ). The second, termed  $N^*$ , represents those nitrogen atoms populating the remaining upper electronic states



( $E = 83285.5 \div 117345 \text{ cm}^{-1}$ ). The relative densities of these two new species are determined by appropriate reaction rates between themselves,  $\text{N}^+$ ,  $\text{e}^-$ , etc, and the electronic states of each are assumed to be in LTE.

As opposed to the second-order LTNE model authors of [95] studied also the first-order LTNE model, which assumes direct ionization of nitrogen from the ground state. It was shown that the second-order LTNE model provides acceptable description of flight data FIRE-II. The first-order and the second order LTNE models are presented in Tables RD.12. These tables contain also kinetic model for air which was used by these authors in [101].

## APPENDIX

### RECOMMENDED DATA FOR CREATION RADIATIVE-COLLISION MODELS OF HIGH TEMPERATURE KINETICS BEHIND SHOCK WAVES IN AIR AND CO<sub>2</sub> – N<sub>2</sub>

Table RD1: Electron-impact dissociation rate coefficients [28]

No. of electronic state	Term	$A_{ex}$ , cm <sup>3</sup> /s	$n$	$T_d$ , K
N <sub>2</sub>				
1	X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.95E-08	0.388	113729
2	A <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	1.43E-07	0.605	40877
3	B <sup>3</sup> Π <sub>g</sub>	1.03E-07	0.533	55172
4	W <sup>3</sup> Δ <sub>u</sub>	1.04E-07	0.534	54897
5	B' <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	4.00E-07	0.811	17490
O <sub>2</sub>				
1	X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	2.04E-08	0.516	59435
2	a <sup>1</sup> Δ <sub>g</sub>	5.13E-08	0.566	47911
3	b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	8.31E-08	0.609	40219
4	c <sup>1</sup> Σ <sub>u</sub> <sup>-</sup>	2.48E-08	0.897	11457
NO				
1	X <sup>2</sup> Π	2.47E-10	0.465	75402
2	a <sup>4</sup> Π	7.34E-10	0.786	19550
3	A <sup>2</sup> Σ <sup>+</sup>	1.90E-09	0.894	11662
4	B <sup>2</sup> Π	6.86E-10	0.632	36639
5	b <sup>4</sup> Σ <sup>-</sup>	6.50E-11	0.661	32630
CO				
1	X <sup>1</sup> Σ <sup>+</sup>	3.50E-10	0.367	129271
2	a <sup>3</sup> Π	5.16E-09	0.519	58742
3	a' <sup>3</sup> Σ <sup>+</sup>	5.49E-09	0.564	48352
4	d <sup>3</sup> Δ	7.03E-09	0.606	40635
5	e <sup>3</sup> Σ <sup>-</sup>	6.51E-09	0.636	36098
6	A <sup>1</sup> Π	7.96E-09	0.644	34864
CN				
1	X <sup>2</sup> Σ <sup>+</sup>	2.17E-09	0.432	88966
2	A <sup>2</sup> Π	9.75E-09	0.464	75564
3	B <sup>2</sup> Σ <sup>+</sup>	3.99E-09	0.549	51576
4	a <sup>4</sup> Σ <sup>+</sup>	2.61E-09	0.599	41890
5	D <sup>2</sup> Π	1.04E-08	0.922	9964
N <sub>2</sub> <sup>+</sup>				
1	X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	3.88E-09	0.408	101519
2	A <sup>2</sup> Π <sub>u</sub>	5.03E-09	0.434	88244
3	B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	1.69E-08	0.498	64608
4	D <sup>2</sup> Π <sub>g</sub>	1.41E-08	0.713	26438

**Table RD2: Rate parameters of dissociation [29]**

	M	$A_d, \text{cm}^3/\text{s}$	$n_d$	$T_d, \text{K}$
$\text{N}_2(X^1\Sigma_g^+) +$	N	4.49E-08	-1.60	113288
	O	4.49E-08	-1.60	113288
	N <sub>2</sub>	1.05E-08	-1.60	113288
	O <sub>2</sub>	1.05E-08	-1.60	113288
	NO	1.05E-08	-1.60	113288
	CO	1.05E-08	-1.60	113288
$\text{N}_2(A^3\Sigma_u^+) +$	N	4.49E-08	-1.60	41057
	O	4.49E-08	-1.60	41057
	N <sub>2</sub>	1.05E-08	-1.60	41057
	O <sub>2</sub>	1.05E-08	-1.60	41057
	NO	1.05E-08	-1.60	41057
	CO	1.05E-08	-1.60	41057
$\text{N}_2(B^3\Pi_g) +$	N	4.49E-08	-1.60	55175
	O	4.49E-08	-1.60	55175
	N <sub>2</sub>	1.05E-08	-1.60	55175
	O <sub>2</sub>	1.05E-08	-1.60	55175
	NO	1.05E-08	-1.60	55175
	CO	1.05E-08	-1.60	55175
$\text{N}_2(W^3\Delta_u) +$	N	4.49E-08	-1.60	54903
	O	4.49E-08	-1.60	54903
	N <sub>2</sub>	1.05E-08	-1.60	54903
	O <sub>2</sub>	1.05E-08	-1.60	54903
	NO	1.05E-08	-1.60	54903
	CO	1.05E-08	-1.60	54903
$\text{N}_2(B'^3\Sigma_u^-) +$	N	4.49E-08	-1.60	45602
	O	4.49E-08	-1.60	45602
	N <sub>2</sub>	1.05E-08	-1.60	45602
	O <sub>2</sub>	1.05E-08	-1.60	45602
	NO	1.05E-08	-1.60	45602
	CO	1.05E-08	-1.60	45602
$\text{O}_2(X^3\Sigma_g^-) +$	N	3.57E-08	-1.50	59392
	O	3.57E-08	-1.50	59392
	N <sub>2</sub>	7.15E-09	-1.50	59392
	O <sub>2</sub>	7.15E-09	-1.50	59392
	NO	7.15E-09	-1.50	59392
	CO	7.15E-09	-1.50	59392
$\text{O}_2(a^1\Delta_g) +$	N	3.57E-08	-1.50	48000
	O	3.57E-08	-1.50	48000
	N <sub>2</sub>	7.15E-09	-1.50	48000
	O <sub>2</sub>	7.15E-09	-1.50	48000
	NO	7.15E-09	-1.50	48000
	CO	7.15E-09	-1.50	48000

Table RD2: (Continuation of the table)

	M	$A_d$ , cm <sup>3</sup> /s	$n_d$	$T_d$ , K
$O_2(b^1\Sigma_g^+)+$	N	3.57E-08	-1.50	40407
	O	3.57E-08	-1.50	40407
	N <sub>2</sub>	7.15E-09	-1.50	40407
	O <sub>2</sub>	7.15E-09	-1.50	40407
	NO	7.15E-09	-1.50	40407
	CO	7.15E-09	-1.50	40407
$O_2(c^1\Sigma_u^-)+$	N	3.57E-08	-1.50	11830
	O	3.57E-08	-1.50	11830
	N <sub>2</sub>	7.15E-09	-1.50	11830
	O <sub>2</sub>	7.15E-09	-1.50	11830
	NO	7.15E-09	-1.50	11830
	CO	7.15E-09	-1.50	11830
$NO(X^2\Pi)+$	N	1.60E-09	0.00	75210
	O	1.60E-09	0.00	75210
	N <sub>2</sub>	2.41E-09	0.00	75210
	O <sub>2</sub>	2.41E-09	0.00	75210
	NO	1.60E-09	0.00	75210
	CO	1.60E-09	0.00	75210
$NO(a^4\Pi)+$	N	1.60E-09	0.00	19991
	O	1.60E-09	0.00	19991
	N <sub>2</sub>	2.41E-09	0.00	19991
	O <sub>2</sub>	2.41E-09	0.00	19991
	NO	1.60E-09	0.00	19991
	CO	1.60E-09	0.00	19991
$NO(A^2\Sigma^+)+$	N	1.60E-09	0.00	12041
	O	1.60E-09	0.00	12041
	N <sub>2</sub>	2.41E-09	0.00	12041
	O <sub>2</sub>	2.41E-09	0.00	12041
	NO	1.60E-09	0.00	12041
	CO	1.60E-09	0.00	12041
$NO(B^2\Pi)+$	N	1.60E-09	0.00	36876
	O	1.60E-09	0.00	36876
	N <sub>2</sub>	2.41E-09	0.00	36876
	O <sub>2</sub>	2.41E-09	0.00	36876
	NO	1.60E-09	0.00	36876
	CO	1.60E-09	0.00	36876
$NO(b^4\Sigma^-)+$	N	1.60E-09	0.00	28089
	O	1.60E-09	0.00	28089
	N <sub>2</sub>	2.41E-09	0.00	28089
	O <sub>2</sub>	2.41E-09	0.00	28089
	NO	1.60E-09	0.00	28089
	CO	1.60E-09	0.00	28089

	M	$A_d, \text{cm}^3/\text{s}$	$n_d$	$T_d, \text{K}$
$\text{CO}(X^1\Sigma^+)+$	N	9.41E-08	-1.00	128755
	O	9.41E-08	-1.00	128755
	N <sub>2</sub>	6.37E-08	-1.00	128755
	O <sub>2</sub>	6.37E-08	-1.00	128755
	NO	6.37E-08	-1.00	128755
	CO	6.37E-08	-1.00	128755
$\text{CO}(a^3\Pi)+$	N	9.41E-08	-1.00	58706
	O	9.41E-08	-1.00	58706
	N <sub>2</sub>	6.37E-08	-1.00	58706
	O <sub>2</sub>	6.37E-08	-1.00	58706
	NO	6.37E-08	-1.00	58706
	CO	6.37E-08	-1.00	58706
$\text{CO}(a'^3\Sigma^+)+$	N	9.41E-08	-1.00	48435
	O	9.41E-08	-1.00	48435
	N <sub>2</sub>	6.37E-08	-1.00	48435
	O <sub>2</sub>	6.37E-08	-1.00	48435
	NO	6.37E-08	-1.00	48435
	CO	6.37E-08	-1.00	48435
$\text{CO}(d^3\Delta)+$	N	9.41E-08	-1.00	40817
	O	9.41E-08	-1.00	40817
	N <sub>2</sub>	6.37E-08	-1.00	40817
	O <sub>2</sub>	6.37E-08	-1.00	40817
	NO	6.37E-08	-1.00	40817
	CO	6.37E-08	-1.00	40817
$\text{CO}(e^3\Sigma^-)+$	N	9.41E-08	-1.00	36342
	O	9.41E-08	-1.00	36342
	N <sub>2</sub>	6.37E-08	-1.00	36342
	O <sub>2</sub>	6.37E-08	-1.00	36342
	NO	6.37E-08	-1.00	36342
	CO	6.37E-08	-1.00	36342
$\text{CO}(A^1\Pi)+$	N	9.41E-08	-1.00	35126
	O	9.41E-08	-1.00	35126
	N <sub>2</sub>	6.37E-08	-1.00	35126
	O <sub>2</sub>	6.37E-08	-1.00	35126
	NO	6.37E-08	-1.00	35126
	CO	6.37E-08	-1.00	35126
$\text{CN}(X^2\Sigma^+)+$	N	4.20E-10	0.00	88672
	O	4.20E-10	0.00	88672
	N <sub>2</sub>	4.20E-10	0.00	88672
	O <sub>2</sub>	4.20E-10	0.00	88672
	NO	4.20E-10	0.00	88672
	CO	4.20E-10	0.00	88672

Table RD2: (Continuation of the table)

	M	$A_d$ , cm <sup>3</sup> /s	$n_d$	$T_d$ , K
CN(A <sup>2</sup> Π)+	N	4.20E-10	0.00	75371
	O	4.20E-10	0.00	75371
	N <sub>2</sub>	4.20E-10	0.00	75371
	O <sub>2</sub>	4.20E-10	0.00	75371
	NO	4.20E-10	0.00	75371
	CO	4.20E-10	0.00	75371
CN(B <sup>2</sup> Σ <sup>+</sup> )+	N	4.20E-10	0.00	51620
	O	4.20E-10	0.00	51620
	N <sub>2</sub>	4.20E-10	0.00	51620
	O <sub>2</sub>	4.20E-10	0.00	51620
	NO	4.20E-10	0.00	51620
	CO	4.20E-10	0.00	51620
CO(a <sup>4</sup> Σ <sup>+</sup> )+	N	4.20E-10	0.00	42056
	O	4.20E-10	0.00	42056
	N <sub>2</sub>	4.20E-10	0.00	42056
	O <sub>2</sub>	4.20E-10	0.00	42056
	NO	4.20E-10	0.00	42056
	CO	4.20E-10	0.00	42056
CO(D <sup>2</sup> Π)+	N	4.20E-10	0.00	10279
	O	4.20E-10	0.00	10279
	N <sub>2</sub>	4.20E-10	0.00	10279
	O <sub>2</sub>	4.20E-10	0.00	10279
	NO	4.20E-10	0.00	10279
	CO	4.20E-10	0.00	10279
N <sub>2</sub> <sup>+</sup> (X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> )+	N	3.01E-14	0.50	101145
	O	3.01E-14	0.50	101145
	N <sub>2</sub>	3.01E-14	0.50	101145
	O <sub>2</sub>	3.01E-14	0.50	101145
	NO	3.01E-14	0.50	101145
	CO	3.01E-14	0.50	101145
N <sub>2</sub> <sup>+</sup> (A <sup>2</sup> Π <sub>u</sub> )+	N	3.01E-13	0.50	87955
	O	3.01E-13	0.50	87955
	N <sub>2</sub>	3.01E-13	0.50	87955
	O <sub>2</sub>	3.01E-13	0.50	87955
	NO	3.01E-13	0.50	87955
	CO	3.01E-13	0.50	87955
N <sub>2</sub> <sup>+</sup> (B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )+	N	9.94E-14	0.50	64512
	O	9.94E-14	0.50	64512
	N <sub>2</sub>	9.94E-14	0.50	64512
	O <sub>2</sub>	9.94E-14	0.50	64512
	NO	9.94E-14	0.50	64512
	CO	9.94E-14	0.50	64512

	M	$A_d, \text{cm}^3/\text{s}$	$n_d$	$T_d, \text{K}$
$\text{N}_2^+(\text{D}^2\Pi_g)+$	N	9.94E-14	0.50	26814
	O	9.94E-14	0.50	26814
	N <sub>2</sub>	9.94E-14	0.50	26814
	O <sub>2</sub>	9.94E-14	0.50	26814
	NO	9.94E-14	0.50	26814
	CO	9.94E-14	0.50	26814

**Table RD3: Fittings of the dissociation rate coefficients in the Arrhenius form [42]**

$$k_d(T) = A_d T^{n_d} \exp(-E_d/T), \text{cm}^3/\text{s}$$

State	$A_d$	$n_d$	$E_d, \text{K}$	State	$A_d$	$n_d$	$E_d, \text{K}$
O <sub>2</sub> X	$5.76 \times 10^{-22}$	3.52	59369.8	N <sub>2</sub> C	$5.14 \times 10^{-21}$	3.27	12892.7
O <sub>2</sub> a	$9.42 \times 10^{-21}$	3.17	48028.2	N <sub>2</sub> <sup>+</sup> X	$8.02 \times 10^{-31}$	5.54	101117.1
O <sub>2</sub> b	$2.94 \times 10^{-19}$	2.81	40561.7	N <sub>2</sub> <sup>+</sup> A	$8.27 \times 10^{-26}$	4.38	88 142.4
O <sub>2</sub> A	$3.49 \times 10^{-13}$	1.49	8997.6	N <sub>2</sub> <sup>+</sup> B	$2.58 \times 10^{-32}$	5.81	64328.3
O <sub>2</sub> B	$2.30 \times 10^{-13}$	1.54	11180.4	N <sub>2</sub> <sup>+</sup> C	$1.31 \times 10^{-28}$	4.93	35906.8
O <sub>2</sub> <sup>+</sup> X	$1.98 \times 10^{-26}$	4.50	77315.9	NOX	$1.74 \times 10^{-26}$	4.52	75389.6
O <sub>2</sub> <sup>+</sup> a	$2.90 \times 10^{-15}$	1.88	30516.6	NOB	$3.56 \times 10^{-15}$	1.90	36991.2
O <sub>2</sub> <sup>+</sup> A	$7.25 \times 10^{-13}$	1.35	19658.5	NOB'	$2.33 \times 10^{-15}$	1.95	16198.0
O <sub>2</sub> <sup>+</sup> b	$8.12 \times 10^{-16}$	2.02	29365.4	NO <sup>+</sup> X	$8.02 \times 10^{-33}$	6.16	125805.4
O <sub>2</sub> X	$2.40 \times 10^{-09}$	0.49	48060.7	NO <sup>+</sup> a	$4.11 \times 10^{-16}$	2.07	50708.3
N <sub>2</sub> X	$4.11 \times 10^{-33}$	6.16	113263.0	NO <sup>+</sup> b	$3.24 \times 10^{-23}$	3.70	51258.7
N <sub>2</sub> A	$6.61 \times 10^{-20}$	2.98	41 669.6	NO <sup>+</sup> b'	$8.36 \times 10^{-18}$	2.46	39056.6
N <sub>2</sub> B	$4.50 \times 10^{-23}$	3.73	55586.8	NO <sup>+</sup> A	$1.84 \times 10^{-20}$	3.05	30780.4

**Table RD4: Fittings of NO and NO<sup>+</sup> excitation rate coefficients in the Arrhenius form [42]**

$$k_{ex}(T) = A_{ex} T^{n_{ex}} \exp(-E_{ex}/T), \text{cm}^3/\text{s}$$

Transition	$A_{ex}$	$n_{ex}$	$E_{ex}, \text{K}$	Transition	$A_{ex}$	$n_{ex}$	$E_{ex}, \text{K}$
NO(X) → NO(A)	$2.75 \times 10^{-12}$	0.51	53387.3	NO(C) → NO(F)	$1.03 \times 10^{-04}$	-1.53	18319.0
NO(X) → NO(B)	$3.17 \times 10^{-11}$	0.36	58 124.2	NO(B') → NO(F)	$7.15 \times 10^{-09}$	-0.87	6407.6
NO(X) → NO(C)	$1.03 \times 10^{-10}$	0.09	66320.9	NO <sup>+</sup> (X) → NO <sup>+</sup> (a)	$5.28 \times 10^{-13}$	1.13	56955.3
NO(X) → NO(B')	$5.64 \times 10^{-07}$	-0.68	83492.5	NO <sup>+</sup> (X) → NO <sup>+</sup> (b)	$6.49 \times 10^{-10}$	0.44	73 869.9
NO(X) → NO(F)	$7.30 \times 10^{-08}$	-0.70	83 624.4	NO <sup>+</sup> (X) → NO <sup>+</sup> (b')	$1.36 \times 10^{-09}$	0.35	81359.4
NO(A) → NO(B)	$4.79 \times 10^{-08}$	-0.62	18838.5	NO <sup>+</sup> (X) → NO <sup>+</sup> (A)	$1.85 \times 10^{-10}$	0.37	94519.6
NO(A) → NO(C)	$2.72 \times 10^{-07}$	-0.80	15549.8	NO <sup>+</sup> (a) → NO <sup>+</sup> (b)	$7.36 \times 10^{-15}$	1.11	7562.3
NO(A) → NO(B')	$1.06 \times 10^{-05}$	-1.29	26096.9	NO <sup>+</sup> (a) → NO <sup>+</sup> (b')	$7.79 \times 10^{-09}$	-0.23	25 194.8
NO(A) → NO(F)	$3.03 \times 10^{-04}$	-1.59	30403.1	NO <sup>+</sup> (a) → NO <sup>+</sup> (A)	$7.89 \times 10^{-08}$	-0.41	28 865.2

NO(B) → NO(C)	$6.61 \times 10^{-09}$	-0.65	13462.9	NO <sup>+</sup> (b) → NO <sup>+</sup> (b')	$2.07 \times 10^{-12}$	0.52	11384.3
NO(B) → NO(B')	$1.43 \times 10^{-08}$	-0.44	19067.4	NO <sup>+</sup> (b) → NO <sup>+</sup> (A)	$6.21 \times 10^{-06}$	-0.91	23615.8
NO(B) → NO(F)	$1.87 \times 10^{-07}$	-1.20	16318.8	NO <sup>+</sup> (b') → NO <sup>+</sup> (A)	$3.92 \times 10^{-08}$	-0.47	11053.1
NO(C) → NO(B')	$6.29 \times 10^{-05}$	-1.58	18650.4				

Table RD5: Fittings of O<sub>2</sub> and O<sub>2</sub><sup>+</sup> excitation rate coefficients in the Arrhenius form [42]

$$k_{ex}(T) = A_{ex} T^{n_{ex}} \exp(-E_{ex}/T), \text{ cm}^3/\text{s}$$

Transition	$A_{ex}$	$n_{ex}$	$E_{ex}$ , K	Transition	$A_{ex}$	$n_{ex}$	$E_{ex}$ , K
O <sub>2</sub> (X) → O <sub>2</sub> (a)	$6.20 \times 10^{-10}$	-0.12	12498.7	O <sub>2</sub> (b) → O <sub>2</sub> (B)	$3.42 \times 10^{-02}$	-2.09	54845.7
O <sub>2</sub> (X) → O <sub>2</sub> (b)	$4.68 \times 10^{-08}$	-0.52	20884.1	O <sub>2</sub> (A) → O <sub>2</sub> (B)	$1.15 \times 10^{-10}$	0.03	21 366.3
O <sub>2</sub> (X) → O <sub>2</sub> (A)	$1.64 \times 10^{-03}$	-1.70	48941.0	O <sub>2</sub> <sup>+</sup> (X) → O <sub>2</sub> <sup>+</sup> (a)	$6.97 \times 10^{-09}$	-0.15	40020.0
O <sub>2</sub> (X) → O <sub>2</sub> (B)	$6.03 \times 10^{-04}$	-1.51	70974.3	O <sub>2</sub> <sup>+</sup> (X) → O <sub>2</sub> <sup>+</sup> (A)	$9.72 \times 10^{-08}$	-0.61	52156.6
O <sub>2</sub> (a) → O <sub>2</sub> (b)	$1.77 \times 10^{-10}$	0.18	9063.7	O <sub>2</sub> <sup>+</sup> (X) → O <sub>2</sub> <sup>+</sup> (b)	$2.51 \times 10^{-07}$	-0.40	65443.1
O <sub>2</sub> (a) → O <sub>2</sub> (A)	$1.33 \times 10^{-01}$	-2.36	39700.1	O <sub>2</sub> <sup>+</sup> (a) → O <sub>2</sub> <sup>+</sup> (A)	$1.20 \times 10^{-03}$	-1.53	15253.9
O <sub>2</sub> (a) → O <sub>2</sub> (B)	$4.34 \times 10^{-02}$	-2.09	61778.8	O <sub>2</sub> <sup>+</sup> (a) → O <sub>2</sub> <sup>+</sup> (b)	$1.34 \times 10^{-11}$	0.49	20323.6
O <sub>2</sub> (b) → O <sub>2</sub> (A)	$1.17 \times 10^{-01}$	-2.39	33034.0	O <sub>2</sub> <sup>+</sup> (A) → O <sub>2</sub> <sup>+</sup> (b)	$1.31 \times 10^{-11}$	0.44	10571.9

Table RD6: Fittings of N<sub>2</sub> and N<sub>2</sub><sup>+</sup> excitation rate coefficients in the Arrhenius form [42]

$$k_{ex}(T) = A_{ex} T^{n_{ex}} \exp(-E_{ex}/T), \text{ cm}^3/\text{s}$$

Transition	$A_{ex}$	$n_{ex}$	$E_{ex}$ , K	Transition	$A_{ex}$	$n_{ex}$	$E_{ex}$ , K
N <sub>2</sub> (X) → N <sub>2</sub> (A)	$5.48 \times 10^{-11}$	0.55	57700.3	N <sub>2</sub> <sup>+</sup> (X) → N <sub>2</sub> (A)	$8.70 \times 10^{-14}$	1.46	8750.3
N <sub>2</sub> (X) → N <sub>2</sub> (B)	$1.89 \times 10^{-10}$	0.50	75287.5	N <sub>2</sub> <sup>+</sup> (X) → N <sub>2</sub> <sup>+</sup> (B)	$1.52 \times 10^{-10}$	0.75	33501.1
N <sub>2</sub> (X) → N <sub>2</sub> (C)	$8.86 \times 10^{-04}$	-1.13	124965.8	N <sub>2</sub> <sup>+</sup> (X) → N <sub>2</sub> <sup>+</sup> (C)	$6.58 \times 10^{-09}$	0.41	85038.3
N <sub>2</sub> (A) → N <sub>2</sub> (B)	$6.47 \times 10^{-13}$	1.25	9229.0	N <sub>2</sub> <sup>+</sup> (A) → N <sub>2</sub> <sup>+</sup> (B)	$2.35 \times 10^{-15}$	1.80	11953.0
N <sub>2</sub> (A) → N <sub>2</sub> (C)	$2.85 \times 10^{-09}$	0.28	46655.0	N <sub>2</sub> <sup>+</sup> (A) → N <sub>2</sub> <sup>+</sup> (C)	$1.32 \times 10^{-07}$	0.11	78403.3
N <sub>2</sub> (B) → N <sub>2</sub> (C)	$1.15 \times 10^{-03}$	-0.99	44385.4	N <sub>2</sub> <sup>+</sup> (B) → N <sub>2</sub> <sup>+</sup> (C)	$3.86 \times 10^{-09}$	0.34	49622.8

Table RD7: Fittings of NO ionization rate coefficients in the Arrhenius form [42]

$$k_i(T) = A_i T^{n_i} \exp(-E_i/T), \text{ cm}^3/\text{s}$$

Transition	$A_i$	$n_i$	$E_i$ , K	Transition	$A_i$	$n_i$	$E_i$ , K
NO(X) → NO <sup>+</sup> (X)	$4.49 \times 10^{-14}$	1.13	95091.7	NO(C) → NO <sup>+</sup> (X)	$4.13 \times 10^{-07}$	-0.35	34906.4
NO(X) → NO <sup>+</sup> (a)	$8.76 \times 10^{-13}$	0.92	176367.4	NO(C) → NO <sup>+</sup> (a)	$1.03 \times 10^{-14}$	1.23	102939.0
NO(X) → NO <sup>+</sup> (b)	$1.94 \times 10^{-11}$	0.57	193172.9	NO(C) → NO <sup>+</sup> (b)	$1.04 \times 10^{-12}$	0.74	112953.6
NO(X) → NO <sup>+</sup> (b')	$6.17 \times 10^{-12}$	0.67	199142.3	NO(C) → NO <sup>+</sup> (b')	$9.33 \times 10^{-14}$	0.94	126544.4
NO(X) → NO <sup>+</sup> (A)	$1.41 \times 10^{-10}$	0.26	213309.7	NO(C) → NO <sup>+</sup> (A)	$1.68 \times 10^{-12}$	0.56	133924.2
NO(A) → NO <sup>+</sup> (X)	$1.36 \times 10^{-07}$	-0.23	46605.8	NO(B') → NO <sup>+</sup> (X)	$4.26 \times 10^{-15}$	1.34	14183.2



NO (A) $\rightarrow$ NO <sup>+</sup> (a)	$1.63 \times 10^{-13}$	0.99	112686.3	NO (B') $\rightarrow$ NO <sup>+</sup> (a)	$3.32 \times 10^{-14}$	1.24	94034.2
NO (A) $\rightarrow$ NO <sup>+</sup> (b)	$5.43 \times 10^{-12}$	0.62	124299.2	NO (B') $\rightarrow$ NO <sup>+</sup> (b)	$3.87 \times 10^{-18}$	2.05	97 574.5
NO (A) $\rightarrow$ NO <sup>+</sup> (b')	$9.45 \times 10^{-13}$	0.74	135980.5	NO (B') $\rightarrow$ NO <sup>+</sup> (b')	$1.23 \times 10^{-13}$	1.05	117057.5
NO (A) $\rightarrow$ NO <sup>+</sup> (A)	$9.96 \times 10^{-12}$	0.42	144942.4	NO (B') $\rightarrow$ NO <sup>+</sup> (A)	$4.63 \times 10^{-17}$	1.70	120200.9
NO (B) $\rightarrow$ NO <sup>+</sup> (X)	$5.24 \times 10^{-12}$	0.54	22788.9	NO (F) $\rightarrow$ NO <sup>+</sup> (X)	$6.67 \times 10^{-07}$	-0.43	20 145.3
NO (B) $\rightarrow$ NO <sup>+</sup> (a)	$6.64 \times 10^{-15}$	1.37	108170.0	NO (F) $\rightarrow$ NO <sup>+</sup> (a)	$8.66 \times 10^{-17}$	1.66	92712.9
NO (B) $\rightarrow$ NO <sup>+</sup> (b)	$9.23 \times 10^{-18}$	1.88	108088.5	NO (F) $\rightarrow$ NO <sup>+</sup> (b)	$1.02 \times 10^{-13}$	0.90	100718.0
NO (B) $\rightarrow$ NO <sup>+</sup> (b')	$4.51 \times 10^{-14}$	1.13	132080.0	NO (F) $\rightarrow$ NO <sup>+</sup> (b')	$1.36 \times 10^{-15}$	1.30	116677.3
NO (B) $\rightarrow$ NO <sup>+</sup> (A)	$9.65 \times 10^{-18}$	1.80	130416.9	NO (F) $\rightarrow$ NO <sup>+</sup> (A)	$5.64 \times 10^{-14}$	0.84	121886.7

**Table RD8: Fittings of O<sub>2</sub> ionization rate coefficients in the Arrhenius form [42]**

$$k_i(T) = A_i T^{n_i} \exp(-E_i/T), \text{ cm}^3/\text{s}$$

Transition	$A_i$	$n_i$	$E_i$ , K	Transition	$A_i$	$n_i$	$E_i$ , K
O <sub>2</sub> (X) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (X)	$3.65 \times 10^{-14}$	1.16	130102.0	O <sub>2</sub> (b) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (A)	$5.17 \times 10^{-09}$	-0.15	178013.5
O <sub>2</sub> (X) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (a)	$1.89 \times 10^{-10}$	0.31	183169.9	O <sub>2</sub> (b) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (b)	$2.96 \times 10^{-10}$	0.16	193117.9
O <sub>2</sub> (X) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (A)	$1.15 \times 10^{-08}$	-0.14	194852.8	O <sub>2</sub> (A) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (X)	$1.09 \times 10^{-24}$	3.44	96481.5
O <sub>2</sub> (X) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (b)	$6.19 \times 10^{-10}$	0.17	210535.6	O <sub>2</sub> (A) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (a)	$1.86 \times 10^{-17}$	1.83	132765.8
O <sub>2</sub> (a) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (X)	$8.87 \times 10^{-15}$	1.21	118458.0	O <sub>2</sub> (A) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (A)	$2.49 \times 10^{-15}$	1.33	145388.8
O <sub>2</sub> (a) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (a)	$8.68 \times 10^{-11}$	0.31	173011.0	O <sub>2</sub> (A) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (b)	$1.59 \times 10^{-19}$	2.27	156744.5
O <sub>2</sub> (a) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (A)	$4.90 \times 10^{-09}$	-0.13	184733.7	O <sub>2</sub> (B) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (X)	$5.73 \times 10^{-26}$	3.76	77005.0
O <sub>2</sub> (a) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (b)	$2.60 \times 10^{-10}$	0.18	200019.5	O <sub>2</sub> (B) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (a)	$1.07 \times 10^{-19}$	2.38	109539.5
O <sub>2</sub> (b) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (X)	$5.83 \times 10^{-15}$	1.23	110703.5	O <sub>2</sub> (B) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (A)	$4.71 \times 10^{-17}$	1.76	122778.5
O <sub>2</sub> (b) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (a)	$1.03 \times 10^{-10}$	0.28	166337.0	O <sub>2</sub> (B) $\rightarrow$ O <sub>2</sub> <sup>+</sup> (b)	$2.21 \times 10^{-21}$	2.72	134636.7

**Table RD9: Fittings of N<sub>2</sub> ionization rate coefficients in the Arrhenius form [42]**

$$k_i(T) = A_i T^{n_i} \exp(-E_i/T), \text{ cm}^3/\text{s}$$

Transition	$A_i$	$n_i$	$E_i$ , K	Transition	$A_i$	$n_i$	$E_i$ , K
N <sub>2</sub> (X) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (X)	$8.58 \times 10^{-12}$	0.72	184300.2	N <sub>2</sub> (B) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (X)	$1.60 \times 10^{-13}$	1.00	87863.1
N <sub>2</sub> (X) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (A)	$1.54 \times 10^{-13}$	1.11	187758.5	N <sub>2</sub> (B) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (A)	$1.01 \times 10^{-11}$	0.62	107537.3
N <sub>2</sub> (X) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (B)	$1.80 \times 10^{-12}$	0.81	217667.8	N <sub>2</sub> (B) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (B)	$1.27 \times 10^{-15}$	1.36	113666.1
N <sub>2</sub> (X) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (C)	$1.51 \times 10^{-13}$	0.94	262404.0	N <sub>2</sub> (B) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (C)	$1.45 \times 10^{-11}$	0.42	189136.4
N <sub>2</sub> (A) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (X)	$5.48 \times 10^{-16}$	1.43	93478.3	N <sub>2</sub> (C) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (X)	$2.43 \times 10^{-15}$	1.52	52847.1
N <sub>2</sub> (A) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (A)	$5.45 \times 10^{-15}$	1.25	111483.2	N <sub>2</sub> (C) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (A)	$7.00 \times 10^{-15}$	1.40	64344.5
N <sub>2</sub> (A) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (B)	$6.03 \times 10^{-18}$	1.77	122005.4	N <sub>2</sub> (C) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (B)	$2.30 \times 10^{-18}$	2.09	82522.5
N <sub>2</sub> (A) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (C)	$1.11 \times 10^{-12}$	0.63	203 145.8	N <sub>2</sub> (C) $\rightarrow$ N <sub>2</sub> <sup>+</sup> (C)	$7.90 \times 10^{-18}$	1.84	142 103.0

**Tables RD10: Radiative life-times of electronic-vibrational states**

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Name of transition = C2\_ax    Total life time = 0.34037E-06 1/s

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Vu= 0	Aul= 0.76170E+05, 1/s	Life Time= 0.13129E-04 s
Vu= 1	Aul= 0.95735E+05, 1/s	Life Time= 0.10445E-04 s
Vu= 2	Aul= 0.11388E+06, 1/s	Life Time= 0.87814E-05 s
Vu= 3	Aul= 0.13098E+06, 1/s	Life Time= 0.76350E-05 s
Vu= 4	Aul= 0.14674E+06, 1/s	Life Time= 0.68147E-05 s
Vu= 5	Aul= 0.16162E+06, 1/s	Life Time= 0.61872E-05 s
Vu= 6	Aul= 0.17526E+06, 1/s	Life Time= 0.57059E-05 s
Vu= 7	Aul= 0.18789E+06, 1/s	Life Time= 0.53222E-05 s
Vu= 8	Aul= 0.19965E+06, 1/s	Life Time= 0.50088E-05 s
Vu= 9	Aul= 0.21043E+06, 1/s	Life Time= 0.47521E-05 s
Vu= 10	Aul= 0.22038E+06, 1/s	Life Time= 0.45376E-05 s
Vu= 11	Aul= 0.22935E+06, 1/s	Life Time= 0.43602E-05 s
Vu= 12	Aul= 0.23751E+06, 1/s	Life Time= 0.42103E-05 s
Vu= 13	Aul= 0.24501E+06, 1/s	Life Time= 0.40815E-05 s
Vu= 14	Aul= 0.25107E+06, 1/s	Life Time= 0.39830E-05 s
Vu= 15	Aul= 0.25627E+06, 1/s	Life Time= 0.39021E-05 s

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Name of transition = C2\_B1A1    Total life time = 0.35790E-05 1/s

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Vu= 0	Aul= 0.70006E+04, 1/s	Life Time= 0.14284E-03 s
Vu= 1	Aul= 0.11343E+05, 1/s	Life Time= 0.88160E-04 s
Vu= 2	Aul= 0.15441E+05, 1/s	Life Time= 0.64763E-04 s
Vu= 3	Aul= 0.19291E+05, 1/s	Life Time= 0.51837E-04 s
Vu= 4	Aul= 0.22858E+05, 1/s	Life Time= 0.43749E-04 s
Vu= 5	Aul= 0.26303E+05, 1/s	Life Time= 0.38019E-04 s
Vu= 6	Aul= 0.29599E+05, 1/s	Life Time= 0.33785E-04 s
Vu= 7	Aul= 0.32737E+05, 1/s	Life Time= 0.30547E-04 s
Vu= 8	Aul= 0.35600E+05, 1/s	Life Time= 0.28090E-04 s
Vu= 9	Aul= 0.38375E+05, 1/s	Life Time= 0.26058E-04 s
Vu= 10	Aul= 0.40858E+05, 1/s	Life Time= 0.24475E-04 s

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Name of transition = C2\_ba    Total life time= 0.69578E-06 1/s

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Vu= 0	Aul= 0.60190E+05, 1/s	Life Time= 0.16614E-04 s
Vu= 1	Aul= 0.70737E+05, 1/s	Life Time= 0.14137E-04 s
Vu= 2	Aul= 0.80341E+05, 1/s	Life Time= 0.12447E-04 s
Vu= 3	Aul= 0.89427E+05, 1/s	Life Time= 0.11182E-04 s
Vu= 4	Aul= 0.98000E+05, 1/s	Life Time= 0.10204E-04 s
Vu= 5	Aul= 0.10603E+06, 1/s	Life Time= 0.94314E-05 s

Vu= 6	Aul= 0.11362E+06, 1/s	Life Time= 0.88012E-05 s
Vu= 7	Aul= 0.12082E+06, 1/s	Life Time= 0.82770E-05 s
Vu= 8	Aul= 0.12751E+06, 1/s	Life Time= 0.78424E-05 s
Vu= 9	Aul= 0.13400E+06, 1/s	Life Time= 0.74627E-05 s
Vu= 10	Aul= 0.14006E+06, 1/s	Life Time= 0.71398E-05 s
Vu= 11	Aul= 0.14577E+06, 1/s	Life Time= 0.68604E-05 s
Vu= 12	Aul= 0.15075E+06, 1/s	Life Time= 0.66336E-05 s

=====  
 Name of transition = C2\_B'1A1 Total life time = 0.65369E-06 1/s  
 =====

Vu= 0	Aul= 0.12450E+06, 1/s	Life Time= 0.80321E-05 s
Vu= 1	Aul= 0.12923E+06, 1/s	Life Time= 0.77381E-05 s
Vu= 2	Aul= 0.13295E+06, 1/s	Life Time= 0.75216E-05 s
Vu= 3	Aul= 0.13597E+06, 1/s	Life Time= 0.73545E-05 s
Vu= 4	Aul= 0.13822E+06, 1/s	Life Time= 0.72349E-05 s
Vu= 5	Aul= 0.14033E+06, 1/s	Life Time= 0.71258E-05 s
Vu= 6	Aul= 0.14229E+06, 1/s	Life Time= 0.70279E-05 s
Vu= 7	Aul= 0.14412E+06, 1/s	Life Time= 0.69387E-05 s
Vu= 8	Aul= 0.14581E+06, 1/s	Life Time= 0.68581E-05 s
Vu= 9	Aul= 0.14745E+06, 1/s	Life Time= 0.67820E-05 s
Vu= 10	Aul= 0.14891E+06, 1/s	Life Time= 0.67156E-05 s

=====  
 Name of transition = C2\_ca Total life time = 0.31883E-08 1/s  
 =====

Vu= 0	Aul= 0.32547E+08, 1/s	Life Time= 0.30725E-07 s
Vu= 1	Aul= 0.32508E+08, 1/s	Life Time= 0.30762E-07 s
Vu= 2	Aul= 0.32070E+08, 1/s	Life Time= 0.31181E-07 s
Vu= 3	Aul= 0.31412E+08, 1/s	Life Time= 0.31835E-07 s
Vu= 4	Aul= 0.30663E+08, 1/s	Life Time= 0.32612E-07 s
Vu= 5	Aul= 0.29815E+08, 1/s	Life Time= 0.33541E-07 s
Vu= 6	Aul= 0.28662E+08, 1/s	Life Time= 0.34890E-07 s
Vu= 7	Aul= 0.27232E+08, 1/s	Life Time= 0.36721E-07 s
Vu= 8	Aul= 0.25403E+08, 1/s	Life Time= 0.39366E-07 s
Vu= 9	Aul= 0.22980E+08, 1/s	Life Time= 0.43515E-07 s
Vu= 10	Aul= 0.20358E+08, 1/s	Life Time= 0.49121E-07 s

=====

Name of transition = C2\_da    Total life time = 0.12088E-07 1/s

-----

Vu= 0	Aul= 0.97949E+07, 1/s	Life Time= 0.10209E-06 s
Vu= 1	Aul= 0.95393E+07, 1/s	Life Time= 0.10483E-06 s
Vu= 2	Aul= 0.92990E+07, 1/s	Life Time= 0.10754E-06 s
Vu= 3	Aul= 0.90091E+07, 1/s	Life Time= 0.11100E-06 s
Vu= 4	Aul= 0.86751E+07, 1/s	Life Time= 0.11527E-06 s
Vu= 5	Aul= 0.82793E+07, 1/s	Life Time= 0.12078E-06 s
Vu= 6	Aul= 0.77520E+07, 1/s	Life Time= 0.12900E-06 s
Vu= 7	Aul= 0.69260E+07, 1/s	Life Time= 0.14438E-06 s
Vu= 8	Aul= 0.56800E+07, 1/s	Life Time= 0.17606E-06 s
Vu= 9	Aul= 0.42837E+07, 1/s	Life Time= 0.23344E-06 s
Vu= 10	Aul= 0.34849E+07, 1/s	Life Time= 0.28695E-06 s

=====

-----

Name of transition = C2\_da    Total life time = 0.50492E-07 1/s

-----

Vu= 0	Aul= 0.13916E+07, 1/s	Life Time= 0.71859E-06 s
Vu= 1	Aul= 0.14520E+07, 1/s	Life Time= 0.68873E-06 s
Vu= 2	Aul= 0.15114E+07, 1/s	Life Time= 0.66162E-06 s
Vu= 3	Aul= 0.15629E+07, 1/s	Life Time= 0.63983E-06 s
Vu= 4	Aul= 0.16110E+07, 1/s	Life Time= 0.62074E-06 s
Vu= 5	Aul= 0.16531E+07, 1/s	Life Time= 0.60492E-06 s
Vu= 6	Aul= 0.16903E+07, 1/s	Life Time= 0.59159E-06 s
Vu= 7	Aul= 0.17206E+07, 1/s	Life Time= 0.58119E-06 s
Vu= 8	Aul= 0.17427E+07, 1/s	Life Time= 0.57383E-06 s
Vu= 9	Aul= 0.13610E+07, 1/s	Life Time= 0.73476E-06 s
Vu= 10	Aul= 0.14053E+07, 1/s	Life Time= 0.71159E-06 s
Vu= 11	Aul= 0.14171E+07, 1/s	Life Time= 0.70567E-06 s
Vu= 12	Aul= 0.12863E+07, 1/s	Life Time= 0.77745E-06 s

=====

-----

Name of transition = C2\_dx    Total life time = 0.11665E-08 1/s

-----

Vu= 0	Aul= 0.68632E+08, 1/s	Life Time= 0.14571E-07 s
Vu= 1	Aul= 0.67078E+08, 1/s	Life Time= 0.14908E-07 s
Vu= 2	Aul= 0.65547E+08, 1/s	Life Time= 0.15256E-07 s
Vu= 3	Aul= 0.63878E+08, 1/s	Life Time= 0.15655E-07 s
Vu= 4	Aul= 0.62110E+08, 1/s	Life Time= 0.16101E-07 s
Vu= 5	Aul= 0.60179E+08, 1/s	Life Time= 0.16617E-07 s
Vu= 6	Aul= 0.58118E+08, 1/s	Life Time= 0.17206E-07 s
Vu= 7	Aul= 0.55871E+08, 1/s	Life Time= 0.17898E-07 s

=====

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Vu= 8  Aul= 0.53484E+08, 1/s  Life Time= 0.18697E-07 s
Vu= 9  Aul= 0.50893E+08, 1/s  Life Time= 0.19649E-07 s
Vu= 10 Aul= 0.48301E+08, 1/s  Life Time= 0.20704E-07 s
Vu= 11 Aul= 0.45834E+08, 1/s  Life Time= 0.21818E-07 s
Vu= 12 Aul= 0.43677E+08, 1/s  Life Time= 0.22896E-07 s
Vu= 13 Aul= 0.41925E+08, 1/s  Life Time= 0.23852E-07 s
Vu= 14 Aul= 0.40163E+08, 1/s  Life Time= 0.24898E-07 s
Vu= 15 Aul= 0.31578E+08, 1/s  Life Time= 0.31668E-07 s
=====

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=====
Name of transition = C2_E1A1  Total life time = 0.18432E-08 1/s
=====

```

```

Vu= 0  Aul= 0.60090E+08, 1/s  Life Time= 0.16642E-07 s
Vu= 1  Aul= 0.59700E+08, 1/s  Life Time= 0.16750E-07 s
Vu= 2  Aul= 0.58930E+08, 1/s  Life Time= 0.16969E-07 s
Vu= 3  Aul= 0.57495E+08, 1/s  Life Time= 0.17393E-07 s
Vu= 4  Aul= 0.55676E+08, 1/s  Life Time= 0.17961E-07 s
Vu= 5  Aul= 0.53188E+08, 1/s  Life Time= 0.18801E-07 s
Vu= 6  Aul= 0.47816E+08, 1/s  Life Time= 0.20913E-07 s
Vu= 7  Aul= 0.40411E+08, 1/s  Life Time= 0.24746E-07 s
Vu= 8  Aul= 0.35388E+08, 1/s  Life Time= 0.28258E-07 s
Vu= 9  Aul= 0.34568E+08, 1/s  Life Time= 0.28928E-07 s
Vu= 10 Aul= 0.39286E+08, 1/s  Life Time= 0.25455E-07 s
=====

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=====
Name of transition = C2_E1D1  Total life time = 0.23343E-07 1/s
=====

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```

Vu= 0  Aul= 0.59509E+07, 1/s  Life Time= 0.16804E-06 s
Vu= 1  Aul= 0.53592E+07, 1/s  Life Time= 0.18660E-06 s
Vu= 2  Aul= 0.48280E+07, 1/s  Life Time= 0.20713E-06 s
Vu= 3  Aul= 0.43540E+07, 1/s  Life Time= 0.22967E-06 s
Vu= 4  Aul= 0.39663E+07, 1/s  Life Time= 0.25213E-06 s
Vu= 5  Aul= 0.36501E+07, 1/s  Life Time= 0.27397E-06 s
Vu= 6  Aul= 0.33889E+07, 1/s  Life Time= 0.29508E-06 s
Vu= 7  Aul= 0.31515E+07, 1/s  Life Time= 0.31731E-06 s
Vu= 8  Aul= 0.29310E+07, 1/s  Life Time= 0.34118E-06 s
Vu= 9  Aul= 0.27292E+07, 1/s  Life Time= 0.36641E-06 s
Vu= 10 Aul= 0.25305E+07, 1/s  Life Time= 0.39517E-06 s
=====

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=====  
Name of transition = C2\_ea    Total life time = 0.40260E-07 1/s  
=====

Vu= 0	Aul= 0.49679E+07, 1/s	Life Time= 0.20129E-06 s
Vu= 1	Aul= 0.36873E+07, 1/s	Life Time= 0.27120E-06 s
Vu= 2	Aul= 0.29552E+07, 1/s	Life Time= 0.33838E-06 s
Vu= 3	Aul= 0.24040E+07, 1/s	Life Time= 0.41598E-06 s
Vu= 4	Aul= 0.20961E+07, 1/s	Life Time= 0.47707E-06 s
Vu= 5	Aul= 0.18912E+07, 1/s	Life Time= 0.52876E-06 s
Vu= 6	Aul= 0.16865E+07, 1/s	Life Time= 0.59296E-06 s
Vu= 7	Aul= 0.14824E+07, 1/s	Life Time= 0.67460E-06 s
Vu= 8	Aul= 0.13919E+07, 1/s	Life Time= 0.71843E-06 s
Vu= 9	Aul= 0.12218E+07, 1/s	Life Time= 0.81848E-06 s
Vu= 10	Aul= 0.10543E+07, 1/s	Life Time= 0.94849E-06 s

=====

=====  
Name of transition = C2m\_A2X2    Total life time = 0.25458E-05 1/s  
=====

Vu= 0	Aul= 0.18070E+05, 1/s	Life Time= 0.55342E-04 s
Vu= 1	Aul= 0.22199E+05, 1/s	Life Time= 0.45046E-04 s
Vu= 2	Aul= 0.26101E+05, 1/s	Life Time= 0.38313E-04 s
Vu= 3	Aul= 0.29797E+05, 1/s	Life Time= 0.33560E-04 s
Vu= 4	Aul= 0.33286E+05, 1/s	Life Time= 0.30043E-04 s
Vu= 5	Aul= 0.36565E+05, 1/s	Life Time= 0.27349E-04 s
Vu= 6	Aul= 0.39815E+05, 1/s	Life Time= 0.25116E-04 s
Vu= 7	Aul= 0.42720E+05, 1/s	Life Time= 0.23408E-04 s
Vu= 8	Aul= 0.45520E+05, 1/s	Life Time= 0.21968E-04 s
Vu= 9	Aul= 0.48181E+05, 1/s	Life Time= 0.20755E-04 s
Vu= 10	Aul= 0.50545E+05, 1/s	Life Time= 0.19784E-04 s

=====

=====  
Name of transition = C2m\_bx    Total life time = 0.74662E-08 1/s  
=====

Vu= 0	Aul= 0.13285E+08, 1/s	Life Time= 0.75274E-07 s
Vu= 1	Aul= 0.13390E+08, 1/s	Life Time= 0.74681E-07 s
Vu= 2	Aul= 0.13496E+08, 1/s	Life Time= 0.74098E-07 s
Vu= 3	Aul= 0.13518E+08, 1/s	Life Time= 0.73978E-07 s
Vu= 4	Aul= 0.13496E+08, 1/s	Life Time= 0.74096E-07 s
Vu= 5	Aul= 0.13346E+08, 1/s	Life Time= 0.74928E-07 s
Vu= 6	Aul= 0.12999E+08, 1/s	Life Time= 0.76926E-07 s

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Vu= 7  Aul= 0.12165E+08, 1/s  Life Time= 0.82205E-07 s
Vu= 8  Aul= 0.10523E+08, 1/s  Life Time= 0.95033E-07 s
Vu= 9  Aul= 0.90371E+07, 1/s  Life Time= 0.11066E-06 s
Vu= 10 Aul= 0.86820E+07, 1/s  Life Time= 0.11518E-06 s
=====

```

```

=====
Name of transition = C2p_ba  Total life time = 0.38943E-06 1/s
=====

```

```

Vu= 0  Aul= 0.11236E+06, 1/s  Life Time= 0.89002E-05 s
Vu= 1  Aul= 0.14353E+06, 1/s  Life Time= 0.69670E-05 s
Vu= 2  Aul= 0.17259E+06, 1/s  Life Time= 0.57942E-05 s
Vu= 3  Aul= 0.19868E+06, 1/s  Life Time= 0.50332E-05 s
Vu= 4  Aul= 0.22217E+06, 1/s  Life Time= 0.45011E-05 s
Vu= 5  Aul= 0.24360E+06, 1/s  Life Time= 0.41051E-05 s
Vu= 6  Aul= 0.26304E+06, 1/s  Life Time= 0.38017E-05 s
Vu= 7  Aul= 0.28045E+06, 1/s  Life Time= 0.35657E-05 s
Vu= 8  Aul= 0.29725E+06, 1/s  Life Time= 0.33642E-05 s
Vu= 9  Aul= 0.31080E+06, 1/s  Life Time= 0.32175E-05 s
Vu= 10 Aul= 0.32336E+06, 1/s  Life Time= 0.30925E-05 s
=====

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```

=====
Name of transition = C2p_bx  Total life time = 0.21562E-07 1/s
=====

```

```

Vu= 0  Aul= 0.65812E+07, 1/s  Life Time= 0.15195E-06 s
Vu= 1  Aul= 0.62335E+07, 1/s  Life Time= 0.16042E-06 s
Vu= 2  Aul= 0.58924E+07, 1/s  Life Time= 0.16971E-06 s
Vu= 3  Aul= 0.55424E+07, 1/s  Life Time= 0.18043E-06 s
Vu= 4  Aul= 0.51759E+07, 1/s  Life Time= 0.19320E-06 s
Vu= 5  Aul= 0.47377E+07, 1/s  Life Time= 0.21107E-06 s
Vu= 6  Aul= 0.40577E+07, 1/s  Life Time= 0.24644E-06 s
Vu= 7  Aul= 0.29945E+07, 1/s  Life Time= 0.33395E-06 s
Vu= 8  Aul= 0.20797E+07, 1/s  Life Time= 0.48083E-06 s
Vu= 9  Aul= 0.18709E+07, 1/s  Life Time= 0.53451E-06 s
Vu= 10 Aul= 0.12120E+07, 1/s  Life Time= 0.82505E-06 s
=====

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=====
Name of transition = CN_AX  Total life time = 0.50233E-06 1/s
=====

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```

Vu= 0  Aul= 0.89101E+05, 1/s  Life Time= 0.11223E-04 s
Vu= 1  Aul= 0.10289E+06, 1/s  Life Time= 0.97188E-05 s
Vu= 2  Aul= 0.11568E+06, 1/s  Life Time= 0.86447E-05 s
Vu= 3  Aul= 0.12764E+06, 1/s  Life Time= 0.78344E-05 s

```

Vu= 4	Aul= 0.13862E+06, 1/s	Life Time= 0.72139E-05 s
Vu= 5	Aul= 0.14898E+06, 1/s	Life Time= 0.67122E-05 s
Vu= 6	Aul= 0.15833E+06, 1/s	Life Time= 0.63160E-05 s
Vu= 7	Aul= 0.16710E+06, 1/s	Life Time= 0.59844E-05 s
Vu= 8	Aul= 0.17509E+06, 1/s	Life Time= 0.57114E-05 s
Vu= 9	Aul= 0.18236E+06, 1/s	Life Time= 0.54838E-05 s
Vu= 10	Aul= 0.18911E+06, 1/s	Life Time= 0.52879E-05 s
Vu= 11	Aul= 0.19520E+06, 1/s	Life Time= 0.51229E-05 s
Vu= 12	Aul= 0.20063E+06, 1/s	Life Time= 0.49842E-05 s

=====  
Name of transition = CN\_BA    Total life time = 0.24720E-06 1/s  
=====

Vu= 0	Aul= 0.78073E+05, 1/s	Life Time= 0.12808E-04 s
Vu= 1	Aul= 0.91812E+05, 1/s	Life Time= 0.10892E-04 s
Vu= 2	Aul= 0.10803E+06, 1/s	Life Time= 0.92568E-05 s
Vu= 3	Aul= 0.12714E+06, 1/s	Life Time= 0.78654E-05 s
Vu= 4	Aul= 0.14959E+06, 1/s	Life Time= 0.66848E-05 s
Vu= 5	Aul= 0.17524E+06, 1/s	Life Time= 0.57064E-05 s
Vu= 6	Aul= 0.20396E+06, 1/s	Life Time= 0.49028E-05 s
Vu= 7	Aul= 0.23400E+06, 1/s	Life Time= 0.42734E-05 s
Vu= 8	Aul= 0.26582E+06, 1/s	Life Time= 0.37619E-05 s
Vu= 9	Aul= 0.29944E+06, 1/s	Life Time= 0.33396E-05 s
Vu= 10	Aul= 0.33135E+06, 1/s	Life Time= 0.30180E-05 s
Vu= 11	Aul= 0.36103E+06, 1/s	Life Time= 0.27699E-05 s
Vu= 12	Aul= 0.38563E+06, 1/s	Life Time= 0.25932E-05 s
Vu= 13	Aul= 0.40369E+06, 1/s	Life Time= 0.24771E-05 s
Vu= 14	Aul= 0.41476E+06, 1/s	Life Time= 0.24111E-05 s
Vu= 15	Aul= 0.41582E+06, 1/s	Life Time= 0.24049E-05 s

=====  
Name of transition = CN\_BX    Total life time = 0.48844E-08 1/s  
=====

Vu= 0	Aul= 0.16371E+08, 1/s	Life Time= 0.61084E-07 s
Vu= 1	Aul= 0.16289E+08, 1/s	Life Time= 0.61392E-07 s
Vu= 2	Aul= 0.16049E+08, 1/s	Life Time= 0.62309E-07 s
Vu= 3	Aul= 0.15720E+08, 1/s	Life Time= 0.63611E-07 s
Vu= 4	Aul= 0.15346E+08, 1/s	Life Time= 0.65162E-07 s
Vu= 5	Aul= 0.14885E+08, 1/s	Life Time= 0.67183E-07 s
Vu= 6	Aul= 0.14355E+08, 1/s	Life Time= 0.69661E-07 s
Vu= 7	Aul= 0.13755E+08, 1/s	Life Time= 0.72699E-07 s
Vu= 8	Aul= 0.13080E+08, 1/s	Life Time= 0.76455E-07 s
Vu= 9	Aul= 0.12377E+08, 1/s	Life Time= 0.80795E-07 s



Vu= 10	Aul= 0.11622E+08, 1/s	Life Time= 0.86044E-07 s
Vu= 11	Aul= 0.10835E+08, 1/s	Life Time= 0.92289E-07 s
Vu= 12	Aul= 0.10021E+08, 1/s	Life Time= 0.99787E-07 s
Vu= 13	Aul= 0.92279E+07, 1/s	Life Time= 0.10837E-06 s
Vu= 14	Aul= 0.77831E+07, 1/s	Life Time= 0.12848E-06 s
Vu= 15	Aul= 0.70150E+07, 1/s	Life Time= 0.14255E-06 s

=====  
 Name of transition = CN\_XA    Total life time = 0.25138E-06 1/s  
 =====

Vu= 0	Aul= 0.45418E+06, 1/s	Life Time= 0.22018E-05 s
Vu= 1	Aul= 0.49289E+06, 1/s	Life Time= 0.20289E-05 s
Vu= 2	Aul= 0.52867E+06, 1/s	Life Time= 0.18915E-05 s
Vu= 3	Aul= 0.55918E+06, 1/s	Life Time= 0.17883E-05 s
Vu= 4	Aul= 0.57345E+06, 1/s	Life Time= 0.17438E-05 s
Vu= 5	Aul= 0.53998E+06, 1/s	Life Time= 0.18519E-05 s
Vu= 6	Aul= 0.41938E+06, 1/s	Life Time= 0.23845E-05 s
Vu= 7	Aul= 0.22685E+06, 1/s	Life Time= 0.44083E-05 s
Vu= 8	Aul= 0.78821E+05, 1/s	Life Time= 0.12687E-04 s
Vu= 9	Aul= 0.47106E+05, 1/s	Life Time= 0.21229E-04 s
Vu= 10	Aul= 0.40337E+05, 1/s	Life Time= 0.24791E-04 s
Vu= 11	Aul= 0.11181E+05, 1/s	Life Time= 0.89441E-04 s
Vu= 12	Aul= 0.59694E+04, 1/s	Life Time= 0.16752E-03 s

=====  
 Name of transition = CN\_XX    Total life time = 0.16363E-03 1/s  
 =====

Vu= 0	Aul= 0.12690E+02, 1/s	Life Time= 0.78805E-01 s
Vu= 1	Aul= 0.36326E+02, 1/s	Life Time= 0.27529E-01 s
Vu= 2	Aul= 0.59900E+02, 1/s	Life Time= 0.16695E-01 s
Vu= 3	Aul= 0.83339E+02, 1/s	Life Time= 0.11999E-01 s
Vu= 4	Aul= 0.10650E+03, 1/s	Life Time= 0.93899E-02 s
Vu= 5	Aul= 0.12932E+03, 1/s	Life Time= 0.77325E-02 s
Vu= 6	Aul= 0.15169E+03, 1/s	Life Time= 0.65924E-02 s
Vu= 7	Aul= 0.17352E+03, 1/s	Life Time= 0.57630E-02 s
Vu= 8	Aul= 0.19472E+03, 1/s	Life Time= 0.51357E-02 s
Vu= 9	Aul= 0.21519E+03, 1/s	Life Time= 0.46470E-02 s
Vu= 10	Aul= 0.23492E+03, 1/s	Life Time= 0.42567E-02 s
Vu= 11	Aul= 0.25383E+03, 1/s	Life Time= 0.39396E-02 s
Vu= 12	Aul= 0.27187E+03, 1/s	Life Time= 0.36783E-02 s
Vu= 13	Aul= 0.28902E+03, 1/s	Life Time= 0.34599E-02 s
Vu= 14	Aul= 0.30522E+03, 1/s	Life Time= 0.32763E-02 s
Vu= 15	Aul= 0.32042E+03, 1/s	Life Time= 0.31209E-02 s
Vu= 16	Aul= 0.33453E+03, 1/s	Life Time= 0.29893E-02 s
Vu= 17	Aul= 0.34755E+03, 1/s	Life Time= 0.28773E-02 s

Vu= 18	Aul= 0.35950E+03, 1/s	Life Time= 0.27817E-02 s
Vu= 19	Aul= 0.37043E+03, 1/s	Life Time= 0.26996E-02 s
Vu= 20	Aul= 0.37957E+03, 1/s	Life Time= 0.26345E-02 s
Vu= 21	Aul= 0.38157E+03, 1/s	Life Time= 0.26208E-02 s
Vu= 22	Aul= 0.35784E+03, 1/s	Life Time= 0.27945E-02 s
Vu= 23	Aul= 0.29845E+03, 1/s	Life Time= 0.33507E-02 s
Vu= 24	Aul= 0.24664E+03, 1/s	Life Time= 0.40544E-02 s
Vu= 25	Aul= 0.19661E+03, 1/s	Life Time= 0.50862E-02 s

=====  
 Name of transition = CO\_a'a    Total life time = 0.68669E-06 1/s  
 =====

Vu= 0	Aul= 0.10733E+05, 1/s	Life Time= 0.93166E-04 s
Vu= 1	Aul= 0.28758E+05, 1/s	Life Time= 0.34773E-04 s
Vu= 2	Aul= 0.48164E+05, 1/s	Life Time= 0.20763E-04 s
Vu= 3	Aul= 0.68751E+05, 1/s	Life Time= 0.14545E-04 s
Vu= 4	Aul= 0.88407E+05, 1/s	Life Time= 0.11311E-04 s
Vu= 5	Aul= 0.10301E+06, 1/s	Life Time= 0.97081E-05 s
Vu= 6	Aul= 0.11440E+06, 1/s	Life Time= 0.87415E-05 s
Vu= 7	Aul= 0.13001E+06, 1/s	Life Time= 0.76915E-05 s
Vu= 8	Aul= 0.14505E+06, 1/s	Life Time= 0.68943E-05 s
Vu= 9	Aul= 0.15984E+06, 1/s	Life Time= 0.62561E-05 s
Vu= 10	Aul= 0.17358E+06, 1/s	Life Time= 0.57611E-05 s
Vu= 11	Aul= 0.18669E+06, 1/s	Life Time= 0.53564E-05 s
Vu= 12	Aul= 0.19886E+06, 1/s	Life Time= 0.50287E-05 s

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 Name of transition = CO\_b3-a3    Total life time = 0.38019E-08 1/s  
 =====

Vu= 0	Aul= 0.17888E+08, 1/s	Life Time= 0.55905E-07 s
Vu= 1	Aul= 0.20158E+08, 1/s	Life Time= 0.49608E-07 s
Vu= 2	Aul= 0.22246E+08, 1/s	Life Time= 0.44952E-07 s
Vu= 3	Aul= 0.24003E+08, 1/s	Life Time= 0.41662E-07 s
Vu= 4	Aul= 0.25247E+08, 1/s	Life Time= 0.39609E-07 s
Vu= 5	Aul= 0.25921E+08, 1/s	Life Time= 0.38579E-07 s
Vu= 6	Aul= 0.25979E+08, 1/s	Life Time= 0.38492E-07 s
Vu= 7	Aul= 0.25852E+08, 1/s	Life Time= 0.38682E-07 s
Vu= 8	Aul= 0.25310E+08, 1/s	Life Time= 0.39510E-07 s
Vu= 9	Aul= 0.25831E+08, 1/s	Life Time= 0.38713E-07 s
Vu= 10	Aul= 0.24593E+08, 1/s	Life Time= 0.40662E-07 s

Name of transition = CO_BA    Total life time = 0.48692E-08 1/s		
Vu= 0	Aul= 0.19103E+08, 1/s	Life Time= 0.52348E-07 s
Vu= 1	Aul= 0.19329E+08, 1/s	Life Time= 0.51735E-07 s
Vu= 2	Aul= 0.19435E+08, 1/s	Life Time= 0.51454E-07 s
Vu= 3	Aul= 0.19340E+08, 1/s	Life Time= 0.51706E-07 s
Vu= 4	Aul= 0.18966E+08, 1/s	Life Time= 0.52726E-07 s
Vu= 5	Aul= 0.18101E+08, 1/s	Life Time= 0.55247E-07 s
Vu= 6	Aul= 0.16378E+08, 1/s	Life Time= 0.61058E-07 s
Vu= 7	Aul= 0.13957E+08, 1/s	Life Time= 0.71648E-07 s
Vu= 8	Aul= 0.11833E+08, 1/s	Life Time= 0.84507E-07 s
Vu= 9	Aul= 0.10645E+08, 1/s	Life Time= 0.93940E-07 s
Vu= 10	Aul= 0.94045E+07, 1/s	Life Time= 0.10633E-06 s
Vu= 11	Aul= 0.78476E+07, 1/s	Life Time= 0.12743E-06 s
Vu= 12	Aul= 0.69958E+07, 1/s	Life Time= 0.14294E-06 s
Vu= 13	Aul= 0.59071E+07, 1/s	Life Time= 0.16929E-06 s
Vu= 14	Aul= 0.42852E+07, 1/s	Life Time= 0.23336E-06 s
Vu= 15	Aul= 0.38439E+07, 1/s	Life Time= 0.26015E-06 s

Name of transition = CO_BX    Total life time = 0.48992E-09 1/s		
Vu= 0	Aul= 0.10471E+08, 1/s	Life Time= 0.95500E-07 s
Vu= 1	Aul= 0.15134E+08, 1/s	Life Time= 0.66076E-07 s
Vu= 2	Aul= 0.22687E+08, 1/s	Life Time= 0.44078E-07 s
Vu= 3	Aul= 0.33445E+08, 1/s	Life Time= 0.29900E-07 s
Vu= 4	Aul= 0.47002E+08, 1/s	Life Time= 0.21276E-07 s
Vu= 5	Aul= 0.62373E+08, 1/s	Life Time= 0.16033E-07 s
Vu= 6	Aul= 0.79434E+08, 1/s	Life Time= 0.12589E-07 s
Vu= 7	Aul= 0.98424E+08, 1/s	Life Time= 0.10160E-07 s
Vu= 8	Aul= 0.11906E+09, 1/s	Life Time= 0.83992E-08 s
Vu= 9	Aul= 0.14135E+09, 1/s	Life Time= 0.70749E-08 s
Vu= 10	Aul= 0.16549E+09, 1/s	Life Time= 0.60427E-08 s
Vu= 11	Aul= 0.19102E+09, 1/s	Life Time= 0.52349E-08 s
Vu= 12	Aul= 0.21879E+09, 1/s	Life Time= 0.45707E-08 s
Vu= 13	Aul= 0.24733E+09, 1/s	Life Time= 0.40433E-08 s
Vu= 14	Aul= 0.27834E+09, 1/s	Life Time= 0.35927E-08 s
Vu= 15	Aul= 0.31083E+09, 1/s	Life Time= 0.32172E-08 s

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Name of transition = CO\_d3-a3 Total life time = 0.22722E-06 1/s

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Vu= 0	Aul= 0.83731E+05, 1/s	Life Time= 0.11943E-04 s
Vu= 1	Aul= 0.12113E+06, 1/s	Life Time= 0.82558E-05 s
Vu= 2	Aul= 0.15471E+06, 1/s	Life Time= 0.64638E-05 s
Vu= 3	Aul= 0.18465E+06, 1/s	Life Time= 0.54158E-05 s
Vu= 4	Aul= 0.21214E+06, 1/s	Life Time= 0.47140E-05 s
Vu= 5	Aul= 0.23744E+06, 1/s	Life Time= 0.42116E-05 s
Vu= 6	Aul= 0.26097E+06, 1/s	Life Time= 0.38318E-05 s
Vu= 7	Aul= 0.28289E+06, 1/s	Life Time= 0.35349E-05 s
Vu= 8	Aul= 0.30185E+06, 1/s	Life Time= 0.33129E-05 s
Vu= 9	Aul= 0.32131E+06, 1/s	Life Time= 0.31122E-05 s
Vu= 10	Aul= 0.33841E+06, 1/s	Life Time= 0.29550E-05 s
Vu= 11	Aul= 0.35433E+06, 1/s	Life Time= 0.28222E-05 s
Vu= 12	Aul= 0.36922E+06, 1/s	Life Time= 0.27084E-05 s
Vu= 13	Aul= 0.38246E+06, 1/s	Life Time= 0.26147E-05 s
Vu= 14	Aul= 0.39363E+06, 1/s	Life Time= 0.25405E-05 s
Vu= 15	Aul= 0.40214E+06, 1/s	Life Time= 0.24867E-05 s

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Name of transition = CO\_e3-a3 Total life time = 0.39893E-06 1/s

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Vu= 0	Aul= 0.69230E+05, 1/s	Life Time= 0.14445E-04 s
Vu= 1	Aul= 0.88624E+05, 1/s	Life Time= 0.11284E-04 s
Vu= 2	Aul= 0.10584E+06, 1/s	Life Time= 0.94478E-05 s
Vu= 3	Aul= 0.12113E+06, 1/s	Life Time= 0.82554E-05 s
Vu= 4	Aul= 0.13454E+06, 1/s	Life Time= 0.74329E-05 s
Vu= 5	Aul= 0.14630E+06, 1/s	Life Time= 0.68351E-05 s
Vu= 6	Aul= 0.15666E+06, 1/s	Life Time= 0.63832E-05 s
Vu= 7	Aul= 0.16538E+06, 1/s	Life Time= 0.60468E-05 s
Vu= 8	Aul= 0.17321E+06, 1/s	Life Time= 0.57732E-05 s
Vu= 9	Aul= 0.17966E+06, 1/s	Life Time= 0.55661E-05 s
Vu= 10	Aul= 0.18531E+06, 1/s	Life Time= 0.53963E-05 s
Vu= 11	Aul= 0.19029E+06, 1/s	Life Time= 0.52551E-05 s
Vu= 12	Aul= 0.19356E+06, 1/s	Life Time= 0.51663E-05 s
Vu= 13	Aul= 0.19665E+06, 1/s	Life Time= 0.50853E-05 s
Vu= 14	Aul= 0.19941E+06, 1/s	Life Time= 0.50148E-05 s
Vu= 15	Aul= 0.20091E+06, 1/s	Life Time= 0.49772E-05 s

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Name of transition = CO_XX    Total life time = 0.34831E-04 1/s		
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Vu= 0	Aul= 0.37464E+02, 1/s	Life Time= 0.26692E-01 s
Vu= 1	Aul= 0.10958E+03, 1/s	Life Time= 0.91259E-02 s
Vu= 2	Aul= 0.17834E+03, 1/s	Life Time= 0.56073E-02 s
Vu= 3	Aul= 0.24354E+03, 1/s	Life Time= 0.41061E-02 s
Vu= 4	Aul= 0.30564E+03, 1/s	Life Time= 0.32718E-02 s
Vu= 5	Aul= 0.36464E+03, 1/s	Life Time= 0.27424E-02 s
Vu= 6	Aul= 0.42047E+03, 1/s	Life Time= 0.23783E-02 s
Vu= 7	Aul= 0.47403E+03, 1/s	Life Time= 0.21096E-02 s
Vu= 8	Aul= 0.52426E+03, 1/s	Life Time= 0.19075E-02 s
Vu= 9	Aul= 0.57201E+03, 1/s	Life Time= 0.17482E-02 s
Vu= 10	Aul= 0.61723E+03, 1/s	Life Time= 0.16201E-02 s
Vu= 11	Aul= 0.65884E+03, 1/s	Life Time= 0.15178E-02 s
Vu= 12	Aul= 0.69862E+03, 1/s	Life Time= 0.14314E-02 s
Vu= 13	Aul= 0.73677E+03, 1/s	Life Time= 0.13573E-02 s
Vu= 14	Aul= 0.77174E+03, 1/s	Life Time= 0.12958E-02 s
Vu= 15	Aul= 0.80389E+03, 1/s	Life Time= 0.12439E-02 s
Vu= 16	Aul= 0.83467E+03, 1/s	Life Time= 0.11981E-02 s
Vu= 17	Aul= 0.86331E+03, 1/s	Life Time= 0.11583E-02 s
Vu= 18	Aul= 0.88946E+03, 1/s	Life Time= 0.11243E-02 s
Vu= 19	Aul= 0.91438E+03, 1/s	Life Time= 0.10936E-02 s
Vu= 20	Aul= 0.93699E+03, 1/s	Life Time= 0.10673E-02 s
Vu= 21	Aul= 0.95731E+03, 1/s	Life Time= 0.10446E-02 s
Vu= 22	Aul= 0.97847E+03, 1/s	Life Time= 0.10220E-02 s
Vu= 23	Aul= 0.99522E+03, 1/s	Life Time= 0.10048E-02 s
Vu= 24	Aul= 0.10129E+04, 1/s	Life Time= 0.98729E-03 s
Vu= 25	Aul= 0.10264E+04, 1/s	Life Time= 0.97431E-03 s
Vu= 26	Aul= 0.10394E+04, 1/s	Life Time= 0.96211E-03 s
Vu= 27	Aul= 0.10514E+04, 1/s	Life Time= 0.95115E-03 s
Vu= 28	Aul= 0.10600E+04, 1/s	Life Time= 0.94341E-03 s
Vu= 29	Aul= 0.10693E+04, 1/s	Life Time= 0.93518E-03 s
Vu= 30	Aul= 0.10762E+04, 1/s	Life Time= 0.92918E-03 s
Vu= 31	Aul= 0.10820E+04, 1/s	Life Time= 0.92421E-03 s
Vu= 32	Aul= 0.10865E+04, 1/s	Life Time= 0.92040E-03 s
Vu= 33	Aul= 0.10837E+04, 1/s	Life Time= 0.92274E-03 s
Vu= 34	Aul= 0.10574E+04, 1/s	Life Time= 0.94572E-03 s
Vu= 35	Aul= 0.94954E+03, 1/s	Life Time= 0.10531E-02 s
Vu= 36	Aul= 0.69411E+03, 1/s	Life Time= 0.14407E-02 s
Vu= 37	Aul= 0.53401E+03, 1/s	Life Time= 0.18726E-02 s
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Name of transition = CO4P    Total life time = 0.46372E-09 1/s		
Vu= 0	Aul= 0.11492E+09, 1/s	Life Time= 0.87020E-08 s
Vu= 1	Aul= 0.11472E+09, 1/s	Life Time= 0.87169E-08 s
Vu= 2	Aul= 0.11426E+09, 1/s	Life Time= 0.87517E-08 s
Vu= 3	Aul= 0.11397E+09, 1/s	Life Time= 0.87745E-08 s
Vu= 4	Aul= 0.11323E+09, 1/s	Life Time= 0.88318E-08 s
Vu= 5	Aul= 0.11213E+09, 1/s	Life Time= 0.89180E-08 s
Vu= 6	Aul= 0.11083E+09, 1/s	Life Time= 0.90225E-08 s
Vu= 7	Aul= 0.10957E+09, 1/s	Life Time= 0.91265E-08 s
Vu= 8	Aul= 0.10818E+09, 1/s	Life Time= 0.92442E-08 s
Vu= 9	Aul= 0.10674E+09, 1/s	Life Time= 0.93685E-08 s
Vu= 10	Aul= 0.10526E+09, 1/s	Life Time= 0.94999E-08 s
Vu= 11	Aul= 0.10372E+09, 1/s	Life Time= 0.96413E-08 s
Vu= 12	Aul= 0.10202E+09, 1/s	Life Time= 0.98024E-08 s
Vu= 13	Aul= 0.10016E+09, 1/s	Life Time= 0.99837E-08 s
Vu= 14	Aul= 0.98197E+08, 1/s	Life Time= 0.10184E-07 s
Vu= 15	Aul= 0.95858E+08, 1/s	Life Time= 0.10432E-07 s
Vu= 16	Aul= 0.93442E+08, 1/s	Life Time= 0.10702E-07 s
Vu= 17	Aul= 0.90542E+08, 1/s	Life Time= 0.11045E-07 s
Vu= 18	Aul= 0.87334E+08, 1/s	Life Time= 0.11450E-07 s
Vu= 19	Aul= 0.83272E+08, 1/s	Life Time= 0.12009E-07 s
Vu= 20	Aul= 0.78111E+08, 1/s	Life Time= 0.12802E-07 s

Name of transition = CO+AX    Total life time = 0.85999E-09 1/s		
Vu= 0	Aul= 0.11492E+09, 1/s	Life Time= 0.87020E-08 s
Vu= 1	Aul= 0.11472E+09, 1/s	Life Time= 0.87170E-08 s
Vu= 2	Aul= 0.11422E+09, 1/s	Life Time= 0.87553E-08 s
Vu= 3	Aul= 0.11326E+09, 1/s	Life Time= 0.88291E-08 s
Vu= 4	Aul= 0.10900E+09, 1/s	Life Time= 0.91747E-08 s
Vu= 5	Aul= 0.10311E+09, 1/s	Life Time= 0.96980E-08 s
Vu= 6	Aul= 0.10332E+09, 1/s	Life Time= 0.96790E-08 s
Vu= 7	Aul= 0.99581E+08, 1/s	Life Time= 0.10042E-07 s
Vu= 8	Aul= 0.99680E+08, 1/s	Life Time= 0.10032E-07 s
Vu= 9	Aul= 0.95917E+08, 1/s	Life Time= 0.10426E-07 s
Vu= 10	Aul= 0.95092E+08, 1/s	Life Time= 0.10516E-07 s

Name of transition = CO+BA    Total life time = 0.41830E-07 1/s		
Vu= 0	Aul= 0.10234E+07, 1/s	Life Time= 0.97710E-06 s
Vu= 1	Aul= 0.11718E+07, 1/s	Life Time= 0.85339E-06 s
Vu= 2	Aul= 0.13212E+07, 1/s	Life Time= 0.75686E-06 s
Vu= 3	Aul= 0.14484E+07, 1/s	Life Time= 0.69040E-06 s
Vu= 4	Aul= 0.15550E+07, 1/s	Life Time= 0.64308E-06 s
Vu= 5	Aul= 0.16351E+07, 1/s	Life Time= 0.61159E-06 s
Vu= 6	Aul= 0.16826E+07, 1/s	Life Time= 0.59433E-06 s
Vu= 7	Aul= 0.16965E+07, 1/s	Life Time= 0.58945E-06 s
Vu= 8	Aul= 0.16809E+07, 1/s	Life Time= 0.59492E-06 s
Vu= 9	Aul= 0.16507E+07, 1/s	Life Time= 0.60582E-06 s
Vu= 10	Aul= 0.16136E+07, 1/s	Life Time= 0.61974E-06 s
Vu= 11	Aul= 0.15753E+07, 1/s	Life Time= 0.63481E-06 s
Vu= 12	Aul= 0.15364E+07, 1/s	Life Time= 0.65088E-06 s
Vu= 13	Aul= 0.14868E+07, 1/s	Life Time= 0.67258E-06 s
Vu= 14	Aul= 0.14386E+07, 1/s	Life Time= 0.69512E-06 s
Vu= 15	Aul= 0.13901E+07, 1/s	Life Time= 0.71938E-06 s

Name of transition = CO+ BX    Total life time = 0.54932E-08 1/s		
Vu= 0	Aul= 0.19431E+08, 1/s	Life Time= 0.51464E-07 s
Vu= 1	Aul= 0.17675E+08, 1/s	Life Time= 0.56578E-07 s
Vu= 2	Aul= 0.16059E+08, 1/s	Life Time= 0.62270E-07 s
Vu= 3	Aul= 0.14667E+08, 1/s	Life Time= 0.68179E-07 s
Vu= 4	Aul= 0.13449E+08, 1/s	Life Time= 0.74354E-07 s
Vu= 5	Aul= 0.12408E+08, 1/s	Life Time= 0.80594E-07 s
Vu= 6	Aul= 0.11510E+08, 1/s	Life Time= 0.86880E-07 s
Vu= 7	Aul= 0.10746E+08, 1/s	Life Time= 0.93061E-07 s
Vu= 8	Aul= 0.10069E+08, 1/s	Life Time= 0.99319E-07 s
Vu= 9	Aul= 0.94849E+07, 1/s	Life Time= 0.10543E-06 s
Vu= 10	Aul= 0.89429E+07, 1/s	Life Time= 0.11182E-06 s
Vu= 11	Aul= 0.84501E+07, 1/s	Life Time= 0.11834E-06 s
Vu= 12	Aul= 0.79485E+07, 1/s	Life Time= 0.12581E-06 s
Vu= 13	Aul= 0.74574E+07, 1/s	Life Time= 0.13410E-06 s
Vu= 14	Aul= 0.70417E+07, 1/s	Life Time= 0.14201E-06 s
Vu= 15	Aul= 0.67054E+07, 1/s	Life Time= 0.14913E-06 s



Name of transition = CO+XX    Total life time = 0.12287E-02 1/s		
Vu= 0	Aul= 0.31763E+01, 1/s	Life Time= 0.31483E+00 s
Vu= 1	Aul= 0.93797E+01, 1/s	Life Time= 0.10661E+00 s
Vu= 2	Aul= 0.16134E+02, 1/s	Life Time= 0.61982E-01 s
Vu= 3	Aul= 0.23277E+02, 1/s	Life Time= 0.42961E-01 s
Vu= 4	Aul= 0.30857E+02, 1/s	Life Time= 0.32408E-01 s
Vu= 5	Aul= 0.38919E+02, 1/s	Life Time= 0.25694E-01 s
Vu= 6	Aul= 0.47322E+02, 1/s	Life Time= 0.21132E-01 s
Vu= 7	Aul= 0.56109E+02, 1/s	Life Time= 0.17823E-01 s
Vu= 8	Aul= 0.64509E+02, 1/s	Life Time= 0.15502E-01 s
Vu= 9	Aul= 0.73079E+02, 1/s	Life Time= 0.13684E-01 s
Vu= 10	Aul= 0.79389E+02, 1/s	Life Time= 0.12596E-01 s
Vu= 11	Aul= 0.87178E+02, 1/s	Life Time= 0.11471E-01 s
Vu= 12	Aul= 0.93076E+02, 1/s	Life Time= 0.10744E-01 s
Vu= 13	Aul= 0.81072E+02, 1/s	Life Time= 0.12335E-01 s
Vu= 14	Aul= 0.56831E+02, 1/s	Life Time= 0.17596E-01 s
Vu= 15	Aul= 0.53535E+02, 1/s	Life Time= 0.18679E-01 s

Name of transition = N21P    Total life time = 0.27816E-06 1/s		
Vu= 0	Aul= 0.74337E+05, 1/s	Life Time= 0.13452E-04 s
Vu= 1	Aul= 0.90941E+05, 1/s	Life Time= 0.10996E-04 s
Vu= 2	Aul= 0.10648E+06, 1/s	Life Time= 0.93914E-05 s
Vu= 3	Aul= 0.12082E+06, 1/s	Life Time= 0.82768E-05 s
Vu= 4	Aul= 0.13403E+06, 1/s	Life Time= 0.74610E-05 s
Vu= 5	Aul= 0.14627E+06, 1/s	Life Time= 0.68365E-05 s
Vu= 6	Aul= 0.15722E+06, 1/s	Life Time= 0.63605E-05 s
Vu= 7	Aul= 0.16708E+06, 1/s	Life Time= 0.59852E-05 s
Vu= 8	Aul= 0.17546E+06, 1/s	Life Time= 0.56993E-05 s
Vu= 9	Aul= 0.18284E+06, 1/s	Life Time= 0.54692E-05 s
Vu= 10	Aul= 0.18900E+06, 1/s	Life Time= 0.52909E-05 s
Vu= 11	Aul= 0.19380E+06, 1/s	Life Time= 0.51599E-05 s
Vu= 12	Aul= 0.19720E+06, 1/s	Life Time= 0.50710E-05 s
Vu= 13	Aul= 0.19947E+06, 1/s	Life Time= 0.50134E-05 s
Vu= 14	Aul= 0.20042E+06, 1/s	Life Time= 0.49895E-05 s
Vu= 15	Aul= 0.19879E+06, 1/s	Life Time= 0.50305E-05 s
Vu= 16	Aul= 0.19452E+06, 1/s	Life Time= 0.51409E-05 s
Vu= 17	Aul= 0.19162E+06, 1/s	Life Time= 0.52188E-05 s
Vu= 18	Aul= 0.18667E+06, 1/s	Life Time= 0.53572E-05 s
Vu= 19	Aul= 0.17221E+06, 1/s	Life Time= 0.58070E-05 s
Vu= 20	Aul= 0.16185E+06, 1/s	Life Time= 0.61784E-05 s



Vu= 21 Aul= 0.15397E+06, 1/s Life Time= 0.64950E-05 s

Name of transition = N22P Total life time = 0.74690E-08 1/s

Vu= 0 Aul= 0.27238E+08, 1/s Life Time= 0.36714E-07 s

Vu= 1 Aul= 0.27236E+08, 1/s Life Time= 0.36716E-07 s

Vu= 2 Aul= 0.27084E+08, 1/s Life Time= 0.36922E-07 s

Vu= 3 Aul= 0.26604E+08, 1/s Life Time= 0.37588E-07 s

Vu= 4 Aul= 0.25725E+08, 1/s Life Time= 0.38872E-07 s

Name of transition = N2\_A3X1 Total life time = 0.10473E+00 1/s

Vu= 0 Aul= 0.48710E+00, 1/s Life Time= 0.20530E+01 s

Vu= 1 Aul= 0.47769E+00, 1/s Life Time= 0.20934E+01 s

Vu= 2 Aul= 0.47053E+00, 1/s Life Time= 0.21253E+01 s

Vu= 3 Aul= 0.46589E+00, 1/s Life Time= 0.21464E+01 s

Vu= 4 Aul= 0.46626E+00, 1/s Life Time= 0.21447E+01 s

Vu= 5 Aul= 0.46761E+00, 1/s Life Time= 0.21385E+01 s

Vu= 6 Aul= 0.46161E+00, 1/s Life Time= 0.21663E+01 s

Vu= 7 Aul= 0.42167E+00, 1/s Life Time= 0.23715E+01 s

Vu= 8 Aul= 0.35447E+00, 1/s Life Time= 0.28211E+01 s

Vu= 9 Aul= 0.36093E+00, 1/s Life Time= 0.27706E+01 s

Vu= 10 Aul= 0.36619E+00, 1/s Life Time= 0.27308E+01 s

Vu= 11 Aul= 0.36766E+00, 1/s Life Time= 0.27199E+01 s

Vu= 12 Aul= 0.38020E+00, 1/s Life Time= 0.26302E+01 s

Vu= 13 Aul= 0.39724E+00, 1/s Life Time= 0.25174E+01 s

Vu= 14 Aul= 0.40061E+00, 1/s Life Time= 0.24962E+01 s

Vu= 15 Aul= 0.42668E+00, 1/s Life Time= 0.23437E+01 s

Vu= 16 Aul= 0.43527E+00, 1/s Life Time= 0.22974E+01 s

Vu= 17 Aul= 0.44365E+00, 1/s Life Time= 0.22540E+01 s

Vu= 18 Aul= 0.46368E+00, 1/s Life Time= 0.21567E+01 s

Vu= 19 Aul= 0.47472E+00, 1/s Life Time= 0.21065E+01 s

Vu= 20 Aul= 0.47668E+00, 1/s Life Time= 0.20978E+01 s

Vu= 21 Aul= 0.48198E+00, 1/s Life Time= 0.20748E+01 s

=====

Name of transition = N2BH1    Total life time = 0.19383E-08 1/s

-----

Vu= 0	Aul= 0.55930E+01, 1/s	Life Time= 0.17879E+00 s
Vu= 1	Aul= 0.51592E+09, 1/s	Life Time= 0.19383E-08 s

=====

=====

Name of transition = N2BH2    Total life time = 0.23481E-10 1/s

-----

Vu= 0	Aul= 0.56997E+09, 1/s	Life Time= 0.17545E-08 s
Vu= 1	Aul= 0.72527E+09, 1/s	Life Time= 0.13788E-08 s
Vu= 2	Aul= 0.88416E+09, 1/s	Life Time= 0.11310E-08 s
Vu= 3	Aul= 0.10322E+10, 1/s	Life Time= 0.96877E-09 s
Vu= 4	Aul= 0.11737E+10, 1/s	Life Time= 0.85204E-09 s
Vu= 5	Aul= 0.13059E+10, 1/s	Life Time= 0.76576E-09 s
Vu= 6	Aul= 0.14238E+10, 1/s	Life Time= 0.70235E-09 s
Vu= 7	Aul= 0.15282E+10, 1/s	Life Time= 0.65435E-09 s
Vu= 8	Aul= 0.16219E+10, 1/s	Life Time= 0.61656E-09 s
Vu= 9	Aul= 0.17034E+10, 1/s	Life Time= 0.58705E-09 s
Vu= 10	Aul= 0.17724E+10, 1/s	Life Time= 0.56421E-09 s
Vu= 11	Aul= 0.18313E+10, 1/s	Life Time= 0.54607E-09 s
Vu= 12	Aul= 0.18782E+10, 1/s	Life Time= 0.53244E-09 s
Vu= 13	Aul= 0.19166E+10, 1/s	Life Time= 0.52175E-09 s
Vu= 14	Aul= 0.19420E+10, 1/s	Life Time= 0.51494E-09 s
Vu= 15	Aul= 0.19691E+10, 1/s	Life Time= 0.50785E-09 s
Vu= 16	Aul= 0.19748E+10, 1/s	Life Time= 0.50639E-09 s
Vu= 17	Aul= 0.19820E+10, 1/s	Life Time= 0.50454E-09 s
Vu= 18	Aul= 0.19813E+10, 1/s	Life Time= 0.50472E-09 s
Vu= 19	Aul= 0.19739E+10, 1/s	Life Time= 0.50661E-09 s
Vu= 20	Aul= 0.19605E+10, 1/s	Life Time= 0.51007E-09 s
Vu= 21	Aul= 0.19426E+10, 1/s	Life Time= 0.51477E-09 s
Vu= 22	Aul= 0.19190E+10, 1/s	Life Time= 0.52111E-09 s
Vu= 23	Aul= 0.18913E+10, 1/s	Life Time= 0.52873E-09 s
Vu= 24	Aul= 0.18610E+10, 1/s	Life Time= 0.53735E-09 s
Vu= 25	Aul= 0.18242E+10, 1/s	Life Time= 0.54819E-09 s

=====

=====

Name of transition = N2\_DB    Total life time = 0.14135E-07 1/s

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Vu= 0	Aul= 0.70747E+08, 1/s	Life Time= 0.14135E-07 s
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=====		
Name of transition = N2P1M    Total life time = 0.57488E-08 1/s		
-----		
Vu= 0	Aul= 0.17062E+08, 1/s	Life Time= 0.58610E-07 s
Vu= 1	Aul= 0.17261E+08, 1/s	Life Time= 0.57935E-07 s
Vu= 2	Aul= 0.17364E+08, 1/s	Life Time= 0.57589E-07 s
Vu= 3	Aul= 0.17346E+08, 1/s	Life Time= 0.57652E-07 s
Vu= 4	Aul= 0.17159E+08, 1/s	Life Time= 0.58279E-07 s
Vu= 5	Aul= 0.16801E+08, 1/s	Life Time= 0.59519E-07 s
Vu= 6	Aul= 0.16225E+08, 1/s	Life Time= 0.61635E-07 s
Vu= 7	Aul= 0.15430E+08, 1/s	Life Time= 0.64809E-07 s
Vu= 8	Aul= 0.14395E+08, 1/s	Life Time= 0.69469E-07 s
Vu= 9	Aul= 0.13164E+08, 1/s	Life Time= 0.75965E-07 s
Vu= 10	Aul= 0.11744E+08, 1/s	Life Time= 0.85149E-07 s
=====		

=====		
Name of transition = N2P_CX    Total life time = 0.41362E-08 1/s		
-----		
Vu= 0	Aul= 0.14604E+08, 1/s	Life Time= 0.68476E-07 s
Vu= 1	Aul= 0.15001E+08, 1/s	Life Time= 0.66661E-07 s
Vu= 2	Aul= 0.15455E+08, 1/s	Life Time= 0.64703E-07 s
Vu= 3	Aul= 0.15903E+08, 1/s	Life Time= 0.62879E-07 s
Vu= 4	Aul= 0.16405E+08, 1/s	Life Time= 0.60957E-07 s
Vu= 5	Aul= 0.16873E+08, 1/s	Life Time= 0.59265E-07 s
Vu= 6	Aul= 0.17257E+08, 1/s	Life Time= 0.57949E-07 s
Vu= 7	Aul= 0.17651E+08, 1/s	Life Time= 0.56654E-07 s
Vu= 8	Aul= 0.18169E+08, 1/s	Life Time= 0.55038E-07 s
Vu= 9	Aul= 0.18435E+08, 1/s	Life Time= 0.54243E-07 s
Vu= 10	Aul= 0.18427E+08, 1/s	Life Time= 0.54269E-07 s
Vu= 11	Aul= 0.18276E+08, 1/s	Life Time= 0.54715E-07 s
Vu= 12	Aul= 0.17753E+08, 1/s	Life Time= 0.56328E-07 s
Vu= 13	Aul= 0.16472E+08, 1/s	Life Time= 0.60707E-07 s
Vu= 14	Aul= 0.31661E+07, 1/s	Life Time= 0.31584E-06 s
Vu= 15	Aul= 0.19203E+07, 1/s	Life Time= 0.52074E-06 s
=====		

=====		
Name of transition = N2PM    Total life time = 0.33429E-06 1/s		
-----		
Vu= 0	Aul= 0.62114E+05, 1/s	Life Time= 0.16099E-04 s
Vu= 1	Aul= 0.74770E+05, 1/s	Life Time= 0.13374E-04 s
Vu= 2	Aul= 0.86446E+05, 1/s	Life Time= 0.11568E-04 s
Vu= 3	Aul= 0.96999E+05, 1/s	Life Time= 0.10309E-04 s
Vu= 4	Aul= 0.10679E+06, 1/s	Life Time= 0.93639E-05 s
=====		

Vu= 5	Aul= 0.11583E+06, 1/s	Life Time= 0.86335E-05 s
Vu= 6	Aul= 0.12399E+06, 1/s	Life Time= 0.80649E-05 s
Vu= 7	Aul= 0.13155E+06, 1/s	Life Time= 0.76018E-05 s
Vu= 8	Aul= 0.13846E+06, 1/s	Life Time= 0.72224E-05 s
Vu= 9	Aul= 0.14509E+06, 1/s	Life Time= 0.68925E-05 s
Vu= 10	Aul= 0.15102E+06, 1/s	Life Time= 0.66216E-05 s
Vu= 11	Aul= 0.15661E+06, 1/s	Life Time= 0.63853E-05 s
Vu= 12	Aul= 0.16189E+06, 1/s	Life Time= 0.61769E-05 s
Vu= 13	Aul= 0.16667E+06, 1/s	Life Time= 0.59999E-05 s
Vu= 14	Aul= 0.17100E+06, 1/s	Life Time= 0.58479E-05 s
Vu= 15	Aul= 0.17518E+06, 1/s	Life Time= 0.57085E-05 s
Vu= 16	Aul= 0.17901E+06, 1/s	Life Time= 0.55863E-05 s
Vu= 17	Aul= 0.18236E+06, 1/s	Life Time= 0.54835E-05 s
Vu= 18	Aul= 0.18571E+06, 1/s	Life Time= 0.53847E-05 s
Vu= 19	Aul= 0.18857E+06, 1/s	Life Time= 0.53031E-05 s
Vu= 20	Aul= 0.19131E+06, 1/s	Life Time= 0.52270E-05 s

=====  
Name of transition = NO\_CA    Total life time = 0.19375E-07 1/s  
=====

Vu= 0	Aul= 0.10311E+08, 1/s	Life Time= 0.96986E-07 s
Vu= 1	Aul= 0.10362E+08, 1/s	Life Time= 0.96507E-07 s
Vu= 2	Aul= 0.10323E+08, 1/s	Life Time= 0.96876E-07 s
Vu= 3	Aul= 0.10324E+08, 1/s	Life Time= 0.96861E-07 s
Vu= 4	Aul= 0.10295E+08, 1/s	Life Time= 0.97135E-07 s

=====  
Name of transition = NO\_DA    Total life time = 0.14918E-07 1/s  
=====

Vu= 0	Aul= 0.14203E+08, 1/s	Life Time= 0.70409E-07 s
Vu= 1	Aul= 0.13912E+08, 1/s	Life Time= 0.71880E-07 s
Vu= 2	Aul= 0.13516E+08, 1/s	Life Time= 0.73987E-07 s
Vu= 3	Aul= 0.13028E+08, 1/s	Life Time= 0.76759E-07 s
Vu= 4	Aul= 0.12376E+08, 1/s	Life Time= 0.80800E-07 s

=====  
Name of transition = NOBET    Total life time = 0.11616E-07 1/s  
=====

Vu= 0	Aul= 0.48606E+06, 1/s	Life Time= 0.20574E-05 s
Vu= 1	Aul= 0.53867E+06, 1/s	Life Time= 0.18564E-05 s
Vu= 2	Aul= 0.59276E+06, 1/s	Life Time= 0.16870E-05 s
Vu= 3	Aul= 0.65812E+06, 1/s	Life Time= 0.15195E-05 s

Vu= 4	Aul= 0.74294E+06, 1/s	Life Time= 0.13460E-05 s
Vu= 5	Aul= 0.86564E+06, 1/s	Life Time= 0.11552E-05 s
Vu= 6	Aul= 0.10525E+07, 1/s	Life Time= 0.95008E-06 s
Vu= 7	Aul= 0.13483E+07, 1/s	Life Time= 0.74169E-06 s
Vu= 8	Aul= 0.18221E+07, 1/s	Life Time= 0.54881E-06 s
Vu= 9	Aul= 0.25708E+07, 1/s	Life Time= 0.38898E-06 s
Vu= 10	Aul= 0.37550E+07, 1/s	Life Time= 0.26631E-06 s
Vu= 11	Aul= 0.55744E+07, 1/s	Life Time= 0.17939E-06 s
Vu= 12	Aul= 0.83525E+07, 1/s	Life Time= 0.11972E-06 s
Vu= 13	Aul= 0.12458E+08, 1/s	Life Time= 0.80271E-07 s
Vu= 14	Aul= 0.18423E+08, 1/s	Life Time= 0.54281E-07 s
Vu= 15	Aul= 0.26849E+08, 1/s	Life Time= 0.37245E-07 s

=====

Name of transition = NOBTS    Total life time = 0.18465E-07 1/s

-----

Vu= 0	Aul= 0.59644E+07, 1/s	Life Time= 0.16766E-06 s
Vu= 1	Aul= 0.62476E+07, 1/s	Life Time= 0.16006E-06 s
Vu= 2	Aul= 0.67368E+07, 1/s	Life Time= 0.14844E-06 s
Vu= 3	Aul= 0.69357E+07, 1/s	Life Time= 0.14418E-06 s
Vu= 4	Aul= 0.70240E+07, 1/s	Life Time= 0.14237E-06 s
Vu= 5	Aul= 0.70638E+07, 1/s	Life Time= 0.14157E-06 s
Vu= 6	Aul= 0.70923E+07, 1/s	Life Time= 0.14100E-06 s
Vu= 7	Aul= 0.70907E+07, 1/s	Life Time= 0.14103E-06 s

=====

Name of transition = NODEL    Total life time = 0.10379E-07 1/s

-----

Vu= 0	Aul= 0.28237E+08, 1/s	Life Time= 0.35414E-07 s
Vu= 1	Aul= 0.21043E+08, 1/s	Life Time= 0.47523E-07 s
Vu= 2	Aul= 0.17103E+08, 1/s	Life Time= 0.58469E-07 s
Vu= 3	Aul= 0.15421E+08, 1/s	Life Time= 0.64845E-07 s
Vu= 4	Aul= 0.14540E+08, 1/s	Life Time= 0.68775E-07 s

=====

Name of transition = NOEPS    Total life time = 0.52977E-08 1/s

-----

Vu= 0	Aul= 0.37671E+08, 1/s	Life Time= 0.26546E-07 s
Vu= 1	Aul= 0.37745E+08, 1/s	Life Time= 0.26493E-07 s
Vu= 2	Aul= 0.37816E+08, 1/s	Life Time= 0.26444E-07 s
Vu= 3	Aul= 0.37835E+08, 1/s	Life Time= 0.26431E-07 s
Vu= 4	Aul= 0.37696E+08, 1/s	Life Time= 0.26528E-07 s

=====

Name of transition = NOGAM    Total life time = 0.21725E-07 1/s

-----

Vu= 0	Aul= 0.48722E+07, 1/s	Life Time= 0.20525E-06 s
Vu= 1	Aul= 0.49225E+07, 1/s	Life Time= 0.20315E-06 s
Vu= 2	Aul= 0.50026E+07, 1/s	Life Time= 0.19989E-06 s
Vu= 3	Aul= 0.50866E+07, 1/s	Life Time= 0.19659E-06 s
Vu= 4	Aul= 0.51685E+07, 1/s	Life Time= 0.19348E-06 s
Vu= 5	Aul= 0.52508E+07, 1/s	Life Time= 0.19045E-06 s
Vu= 6	Aul= 0.52895E+07, 1/s	Life Time= 0.18905E-06 s
Vu= 7	Aul= 0.52738E+07, 1/s	Life Time= 0.18962E-06 s
Vu= 8	Aul= 0.51633E+07, 1/s	Life Time= 0.19368E-06 s

=====

=====

Name of transition = NOP\_AX    Total life time = 0.32641E-08 1/s

-----

Vu= 0	Aul= 0.18463E+08, 1/s	Life Time= 0.54164E-07 s
Vu= 1	Aul= 0.18517E+08, 1/s	Life Time= 0.54005E-07 s
Vu= 2	Aul= 0.18564E+08, 1/s	Life Time= 0.53867E-07 s
Vu= 3	Aul= 0.18609E+08, 1/s	Life Time= 0.53737E-07 s
Vu= 4	Aul= 0.18647E+08, 1/s	Life Time= 0.53627E-07 s
Vu= 5	Aul= 0.18709E+08, 1/s	Life Time= 0.53450E-07 s
Vu= 6	Aul= 0.18780E+08, 1/s	Life Time= 0.53249E-07 s
Vu= 7	Aul= 0.18881E+08, 1/s	Life Time= 0.52964E-07 s
Vu= 8	Aul= 0.18995E+08, 1/s	Life Time= 0.52645E-07 s
Vu= 9	Aul= 0.19138E+08, 1/s	Life Time= 0.52253E-07 s
Vu= 10	Aul= 0.19306E+08, 1/s	Life Time= 0.51798E-07 s
Vu= 11	Aul= 0.19500E+08, 1/s	Life Time= 0.51282E-07 s
Vu= 12	Aul= 0.19729E+08, 1/s	Life Time= 0.50686E-07 s
Vu= 13	Aul= 0.19956E+08, 1/s	Life Time= 0.50110E-07 s
Vu= 14	Aul= 0.20200E+08, 1/s	Life Time= 0.49506E-07 s
Vu= 15	Aul= 0.20366E+08, 1/s	Life Time= 0.49102E-07 s

=====

=====

Name of transition = O2P1M    Total life time = 0.12837E-06 1/s

-----

Vu= 0	Aul= 0.68752E+06, 1/s	Life Time= 0.14545E-05 s
Vu= 1	Aul= 0.68071E+06, 1/s	Life Time= 0.14690E-05 s
Vu= 2	Aul= 0.66680E+06, 1/s	Life Time= 0.14997E-05 s
Vu= 3	Aul= 0.64640E+06, 1/s	Life Time= 0.15470E-05 s
Vu= 4	Aul= 0.62105E+06, 1/s	Life Time= 0.16102E-05 s
Vu= 5	Aul= 0.59077E+06, 1/s	Life Time= 0.16927E-05 s
Vu= 6	Aul= 0.55732E+06, 1/s	Life Time= 0.17943E-05 s

Vu= 7	Aul= 0.52055E+06, 1/s	Life Time= 0.19210E-05 s
Vu= 8	Aul= 0.48243E+06, 1/s	Life Time= 0.20728E-05 s
Vu= 9	Aul= 0.44296E+06, 1/s	Life Time= 0.22575E-05 s
Vu= 10	Aul= 0.40313E+06, 1/s	Life Time= 0.24806E-05 s
Vu= 11	Aul= 0.36452E+06, 1/s	Life Time= 0.27433E-05 s
Vu= 12	Aul= 0.32525E+06, 1/s	Life Time= 0.30746E-05 s
Vu= 13	Aul= 0.28609E+06, 1/s	Life Time= 0.34954E-05 s
Vu= 14	Aul= 0.25720E+06, 1/s	Life Time= 0.38880E-05 s
Vu= 15	Aul= 0.25756E+06, 1/s	Life Time= 0.38826E-05 s

=====  
 Name of transition = O2P2M    Total life time = 0.39941E-07 1/s  
 =====

Vu= 0	Aul= 0.16726E+07, 1/s	Life Time= 0.59785E-06 s
Vu= 1	Aul= 0.16406E+07, 1/s	Life Time= 0.60953E-06 s
Vu= 2	Aul= 0.16042E+07, 1/s	Life Time= 0.62335E-06 s
Vu= 3	Aul= 0.15616E+07, 1/s	Life Time= 0.64038E-06 s
Vu= 4	Aul= 0.14839E+07, 1/s	Life Time= 0.67389E-06 s
Vu= 5	Aul= 0.13588E+07, 1/s	Life Time= 0.73593E-06 s
Vu= 6	Aul= 0.13109E+07, 1/s	Life Time= 0.76282E-06 s
Vu= 7	Aul= 0.12621E+07, 1/s	Life Time= 0.79234E-06 s
Vu= 8	Aul= 0.12165E+07, 1/s	Life Time= 0.82201E-06 s
Vu= 9	Aul= 0.11637E+07, 1/s	Life Time= 0.85934E-06 s
Vu= 10	Aul= 0.11339E+07, 1/s	Life Time= 0.88188E-06 s
Vu= 11	Aul= 0.10801E+07, 1/s	Life Time= 0.92587E-06 s
Vu= 12	Aul= 0.10365E+07, 1/s	Life Time= 0.96482E-06 s
Vu= 13	Aul= 0.10041E+07, 1/s	Life Time= 0.99589E-06 s
Vu= 14	Aul= 0.95998E+06, 1/s	Life Time= 0.10417E-05 s
Vu= 15	Aul= 0.91168E+06, 1/s	Life Time= 0.10969E-05 s
Vu= 16	Aul= 0.87143E+06, 1/s	Life Time= 0.11475E-05 s
Vu= 17	Aul= 0.83564E+06, 1/s	Life Time= 0.11967E-05 s
Vu= 18	Aul= 0.79723E+06, 1/s	Life Time= 0.12543E-05 s
Vu= 19	Aul= 0.75519E+06, 1/s	Life Time= 0.13242E-05 s
Vu= 20	Aul= 0.70956E+06, 1/s	Life Time= 0.14093E-05 s
Vu= 21	Aul= 0.66655E+06, 1/s	Life Time= 0.15003E-05 s

=====  
 Name of transition = O2SR    Total life time = 0.37046E-08 1/s  
 =====

Vu= 0	Aul= 0.18202E+08, 1/s	Life Time= 0.54938E-07 s
Vu= 1	Aul= 0.19094E+08, 1/s	Life Time= 0.52373E-07 s
Vu= 2	Aul= 0.19324E+08, 1/s	Life Time= 0.51748E-07 s
Vu= 3	Aul= 0.19221E+08, 1/s	Life Time= 0.52027E-07 s

Vu= 4	Aul= 0.19953E+08, 1/s	Life Time= 0.50118E-07 s
Vu= 5	Aul= 0.19957E+08, 1/s	Life Time= 0.50108E-07 s
Vu= 6	Aul= 0.20284E+08, 1/s	Life Time= 0.49299E-07 s
Vu= 7	Aul= 0.19989E+08, 1/s	Life Time= 0.50028E-07 s
Vu= 8	Aul= 0.19651E+08, 1/s	Life Time= 0.50888E-07 s
Vu= 9	Aul= 0.19117E+08, 1/s	Life Time= 0.52310E-07 s
Vu= 10	Aul= 0.18092E+08, 1/s	Life Time= 0.55272E-07 s
Vu= 11	Aul= 0.16763E+08, 1/s	Life Time= 0.59655E-07 s
Vu= 12	Aul= 0.15255E+08, 1/s	Life Time= 0.65554E-07 s
Vu= 13	Aul= 0.13513E+08, 1/s	Life Time= 0.74003E-07 s
Vu= 14	Aul= 0.11519E+08, 1/s	Life Time= 0.86816E-07 s

Table RD11. Data base on electronic kinetics obtained at analyses of experimental data on shock waves [92]

Relaxation time coefficient

Process	M	A	n	B
$O_2(v=1)+M$	$N_2$	$4.66 \times 10^{-36}$	5.99	511.1
	$O_2$	$1.1 \times 10^{-25}$	4.235	354.0
	NO	$3.2 \times 10^{-41}$	6.875	592.6
	N	$1.4 \times 10^{-37}$	6.298	528.7
	O	$8.9 \times 10^{-29}$	4.862	353.2
$N_2(v=1)+M$	$N_2$	$3.3 \times 10^{-29}$	4.555	523.9
	$O_2$	$7.6 \times 10^{-44}$	7.104	717.8
	NO	$1.0 \times 10^{-43}$	7.088	712.9
	N	$5.0 \times 10^{-40}$	6.446	848.6
	O	$7.6 \times 10^{-41}$	6.291	662.3

Reactions of dissociation

Reaction	M	$k_0, \text{cm}^3/\text{mol} \cdot \text{s}$
$N_2(v)+M \rightarrow N+N+M$	$N_2$	$4.9 \times 10^{17} \cdot T^{-0.5} \cdot \exp(-113200/T)$
	N	$7.4 \times 10^{18} \cdot T^{-0.5} \cdot \exp(-113200/T)$
	O, $O_2$ , NO	$1.8 \times 10^{17} \cdot T^{-0.5} \cdot \exp(-113200/T)$
	e	$8.1 \times 10^{19} \cdot T_e^{-1.28} \cdot \exp(-113200/T_e)$
$O_2(v)+M \rightarrow O+O+M$	$O_2$	$3.25 \times 10^{19} \cdot T^{-1} \cdot \exp(-59380/T)$
	O	$8.10 \times 10^{19} \cdot T^{-1} \cdot \exp(-59380/T)$
	N, $N_2$ , NO	$6.15 \times 10^{18} \cdot T^{-1} \cdot \exp(-59380/T)$
	e	$1.0 \times 10^{-25} \cdot T_e^{7.9} \cdot \exp(-70760/T_e)$
$O_2(v)+M \rightarrow O+O+M$	$N_2, O_2, N, O, NO$	$4.0 \times 10^{20} \cdot T^{-1.5} \cdot \exp(-75400/T)$
	e	$4.68 \times 10^9 \cdot T_e^{1.34} \cdot \exp(-78530/T_e)$



**Reactions of ionization**

Reaction	$k_{f,r}, \text{cm}^3/\text{mol}\cdot\text{s}$
$\text{N} + \text{O} \rightarrow \text{NO}^+ + \text{e}$	$k_r = 2.6 \times 10^{19} \cdot T_e^{-1}$
$\text{N} + \text{N} \rightarrow \text{N}_2^+ + \text{e}$	$k_r = 5.0 \times 10^{18} \cdot T_e^{-1/2}$
$\text{O} + \text{O} \rightarrow \text{O}_2^+ + \text{e}$	$k_r = 5.0 \times 10^{19} \cdot T_e^{-1}$
$\text{NO} + \text{e} \rightarrow \text{NO}^+ + \text{e} + \text{e}$	$k_f = 6.5 \times 10^{23} \cdot T_e^{-1.7} \cdot \exp(-107370/T_e)$
$\text{N}_2 + \text{e} \rightarrow \text{N}_2^+ + \text{e} + \text{e}$	$k_f = 4.5 \times 10^{-7} \cdot T_e^5 \cdot \exp(-118840/T_e)$
$\text{O} + \text{e} \rightarrow \text{O}^+ + \text{e} + \text{e}$	$k_f = 5.2 \times 10^{12} \cdot T_e^{0.67} \cdot \exp(-157980/T_e)$
$\text{O}_2 + \text{e} \rightarrow \text{O}_2^+ + \text{e} + \text{e}$	$k_f = 1.0 \times 10^{-13} \cdot T_e^6 \cdot \exp(-140150/T_e)$
$\text{N} + \text{e} \rightarrow \text{N}^+ + \text{e} + \text{e}$	$k_f = 1.8 \times 10^{13} \cdot T_e^{0.6} \cdot \exp(-168770/T_e)$

Rate constant coefficients for reaction  $k_{vv'}(T_e) = AT_e^n \exp(-C/T_e)$

$v$	0	0	1	0	1	2	0	1	2	3
$v'$	1	2	2	3	3	3	4	4	4	4
$A$	83	63	116	58	169	35	49	147	24	54
$n$	-0.5	-1.1	-1.3	-1.5	-1.4	-1.0	-1.5	-1.5	-1.0	-1.2
$C$	1.7	1.9	2.0	2.3	2.0	1.5	2.4	2.1	1.4	1.3

$A$  is in  $10^{-10} \text{cm}^3/\text{s}$ ;  $T_e$  and  $C$  are in eV

**Charge-exchange reactions**

Reaction	$k_f, \text{cm}^3/\text{mol}\cdot\text{s}$
$\text{O}_2^+ + \text{N}_2 \rightarrow \text{O}_2 + \text{N}_2^+$	$9.9 \times 10^{12} \cdot \exp(-407070/T)$
$\text{NO}^+ + \text{N}_2 \rightarrow \text{NO} + \text{N}_2^+$	$3.8 \times 10^{15} \cdot \exp(-73230/T)$
$\text{O}_2^+ + \text{N} \rightarrow \text{O}_2 + \text{N}^+$	$8.7 \times 10^{13} \cdot T_e^{0.14} \cdot \exp(-28600/T)$
$\text{O}_2 + \text{O}^+ \rightarrow \text{O}_2^+ + \text{O}$	$6.45 \times 10^{14} \cdot T^{0.7}$
$\text{O}^+ + \text{N}_2 \rightarrow \text{O} + \text{N}_2^+$	$9.0 \times 10^{11} \cdot T^{0.36} \cdot \exp(-22800/T)$
$\text{NO}^+ + \text{O} \rightarrow \text{NO} + \text{O}^+$	$1.82 \times 10^{13} \cdot \exp(-50130/T)$
$\text{NO}^+ + \text{O}_2 \rightarrow \text{NO} + \text{O}_2^+$	$2.4 \times 10^{13} \cdot \exp(-32600/T)$
$\text{N}_2^+ + \text{O} \rightarrow \text{NO} + \text{N}^+$	$1.8 \times 10^{14} \cdot \exp(-25760/T)$
$\text{N}_2 + \text{O}^+ \rightarrow \text{NO} + \text{N}$	$2.2 \times 10^{14}/T$
$\text{NO}^+ + \text{N} \rightarrow \text{O} + \text{N}_2^+$	$7.2 \times 10^{13} \cdot \exp(-35500/T)$
$\text{NO}^+ + \text{O} \rightarrow \text{O}_2 + \text{N}^+$	$10^{12} \cdot \sqrt{T} \cdot \exp(-77200/T)$
$\text{NO} + \text{O}^+ \rightarrow \text{O}_2 + \text{N}^+$	$1.4 \times 10^5 \cdot T^{19} \cdot \exp(-15300/T)$

**Reactions of NO excited states formation**

Reaction	$k_f, \text{cm}^3/\text{mol}\cdot\text{s}$ or $\text{cm}^6/\text{mol}^2\cdot\text{s}$
$\text{N} + \text{O} + \text{N}_2 \rightarrow \text{NO}(\text{A}) + \text{N}_2$	$7.7 \times 10^{13} \cdot (T/300)^{-1.24}$
$\text{N} + \text{O} + \text{N}_2 \rightarrow \text{NO}(\text{B}) + \text{N}_2$	$1.9 \times 10^{13} \cdot (T/300)^{-1.4}$
$\text{N} + \text{O} \rightarrow \text{NO}(\text{A})$	$7.1 \times 10^6 \cdot (T/300)^{-0.35}$
$\text{N} + \text{O} \rightarrow \text{NO}(\text{C})$	$4.1 \times 10^6 \cdot (T/300)^{-0.35}$
$\text{NO}(\text{A}) + M \rightarrow \text{NO}(\text{X}) + M$	$5.20 \times 10^{12} \cdot T^{0.5}$
$\text{NO}(\text{B}) + M \rightarrow \text{NO}(\text{X}) + M$	$6.40 \times 10^{12} \cdot T^{0.5}$

$\text{NO}(\text{C}) + M \rightarrow \text{NO}(\text{X}) + M$	$7.56 \times 10^{12} \cdot T^{0.5}$
$\text{NO}(\text{X}) + e \rightarrow \text{NO}(\text{A}) + e$	$7.20 \times 10^{13} \cdot T_e^{0.6} \cdot \exp(-63500/T_e)$
$\text{NO}(\text{X}) + e \rightarrow \text{NO}(\text{B}) + e$	$6.10 \times 10^{13} \cdot T_e^{0.6} \cdot \exp(-65700/T_e)$
$\text{NO}(\text{X}) + e \rightarrow \text{NO}(\text{C}) + e$	$8.40 \times 10^{13} \cdot T_e^{0.6} \cdot \exp(-74300/T_e)$
$\text{NO}(\text{A}) + e \rightarrow \text{NO}(\text{B}) + e$	$1.20 \times 10^{15}$ (estimation)
$\text{NO}(\text{B}) + e \rightarrow \text{NO}(\text{C}) + e$	$4.10 \times 10^{15}$ (estimation)
$\text{NO}(\text{A}) \rightarrow \text{NO}(\text{X}) + h\nu(\gamma)$	$\tau = 0.2 \text{ } \mu\text{s}$
$\text{NO}(\text{B}) \rightarrow \text{NO}(\text{X}) + h\nu(\beta)$	$\tau = 3.0 \text{ } \mu\text{s}$
$\text{NO}(\text{C}) \rightarrow \text{NO}(\text{X}) + h\nu(\delta)$	$\tau = 30 \text{ } \mu\text{s}$

**Reactions of  $\text{N}_2(\text{AS}_u^+)$  formation**

Reaction	$k_f, \text{cm}^3/\text{mol} \cdot \text{s}$ or $\text{cm}^6/\text{mol}^2 \cdot \text{s}$
$\text{N}_2(\text{X}) + \text{N}_2 \rightarrow \text{N}_2(\text{A}) + \text{N}_2$	$1.1 \times 10^{12} \cdot T^{-0.5} \cdot \exp(-71600/T)$
$\text{N}_2(\text{X}) + \text{N} \rightarrow \text{N}_2(\text{A}) + \text{N}$	$1.2 \times 10^{17} \cdot T^{-1.5} \cdot \exp(-71600/T)$
$\text{N}_2(\text{X}) + \text{O} \rightarrow \text{N}_2(\text{A}) + \text{O}$	$7.2 \times 10^{16} \cdot T^{-1.5} \cdot \exp(-71600/T)$
$\text{N}_2(\text{X}) + \text{O}_2 \rightarrow \text{N}_2(\text{A}) + \text{O}_2$	$6.0 \times 10^{15} \cdot T^{-1.5} \cdot \exp(-71600/T)$
$\text{N} + \text{N} + \text{N}_2 \rightarrow \text{N}_2(\text{A}) + \text{N}_2$	$0.8 \times 10^{17} \cdot T^{-0.8}$
$\text{N} + \text{N} \rightarrow \text{N}_2(\text{A})$	$4.9 \times 10^7 \cdot T^{-0.35}$
$\text{N}_2(\text{A}) + \text{N}_2(\text{A}) \rightarrow \text{N}_2(\text{B}) + \text{N}_2(\text{X}, v)$	$7.4 \times 10^{14}$
$\text{N}_2(\text{X}) + e \rightarrow \text{N}_2(\text{A}) + e$	$6.14 \times 10^{15} \cdot \exp(-71600/T_e)$
$\text{N}_2(\text{A}) + e \rightarrow \text{N}_2(\text{B}) + e$	$1.81 \times 10^{14}$

**Reactions of  $\text{N}_2^+(\text{B}^2\text{S}_u^+)$  formation**

Reaction	$k_f, \text{cm}^3/\text{mol} \cdot \text{s}$
$\text{N}_2(\text{X}, v > 12) + \text{N}_2^+(\text{X}) \rightarrow \text{N}_2^+(\text{B}) + \text{N}_2(\text{X}, v' = 0)$	$1.5 \times 10^{14} \cdot \exp(-800/T)$
$\text{N}_2^+(\text{X}) + e \rightarrow \text{N}_2^+(\text{A}) + e$	$4.3 \times 10^{13} \cdot \exp(-13300/T)$
$\text{N}_2^+(\text{X}) + e \rightarrow \text{N}_2^+(\text{B}) + e$	$5.6 \times 10^{15} \cdot T_e^{-0.5} \cdot \exp(-36800/T_e)$
$\text{N}_2^+(\text{A}) + e \rightarrow \text{N}_2^+(\text{B}) + e$	$6.1 \times 10^{14} \cdot \exp(-23500/T_e)$
$\text{N}_2^+(\text{B}) \rightarrow \text{N}_2^+(\text{X}) + h\nu$	$\tau = 65 \text{ ns}$

**Table RD12. Data base on electronic kinetics obtained at analyses of flight data FIRE-II [93]**

**Reaction system for the first-order LTNE model [93]**

Reaction	<b>A</b>	<b>B</b>	<b>E</b>
$\text{N}_2 + \text{N} = 2\text{N} + \text{N}$	<b><math>4.085 \times 10^{22}</math></b>	<b>-1.5</b>	<b>113 100</b>
$\text{N}_2 + \text{N}_2 = 2\text{N} + \text{N}_2$	<b><math>4.70 \times 10^{17}</math></b>	<b>-0.5</b>	<b>113 100</b>
$\text{N}_2 + e^- = 2\text{N}^* + e^-$	<b><math>3.00 \times 10^{24}</math></b>	<b>-1.6</b>	<b>113 100</b>
$\text{N}_2 + \text{N}^+ = \text{N}_2^+ + \text{N}$	<b><math>1.00 \times 10^{12}</math></b>	<b>0.5</b>	<b>12 200</b>
$\text{N} + \text{N} = \text{N}_2^+ + e^-$	<b><math>1.40 \times 10^{13}</math></b>	<b>0.0</b>	<b>67 800</b>
$\text{N} + e^- = \text{N}^+ + 2e^-$	<b><math>4.16 \times 10^{13}</math></b>	<b>0.5</b>	<b>120 000</b>

$N + N = N + N^+ + e^-$	$2.34 \times 10^{11}$	<b>0.5</b>	<b>120 000</b>
$N + N^+ = 2N^+ + e^-$	$2.34 \times 10^{11}$	<b>0.5</b>	<b>120 000</b>

Rates in the form  $k_f = AT^B \exp(-E/T)$ ;  $T = T_e$  in electron impact reactions.

**Reaction system for the second-order LTNE model [93]**

<b>Reaction</b>	<b>A</b>	<b>B</b>	<b>E</b>
$N_2 + N = 2N_g + N$	$4.085 \times 10^{22}$	<b>-1.5</b>	<b>113 100</b>
$N_2 + N_2 = 2N_g + N_2$	$4.70 \times 10^{17}$	<b>-0.5</b>	<b>113 100</b>
$N_2 + N^+ = 2N_g + N^+$	$1.90 \times 10^{17}$	<b>-0.5</b>	<b>113 100</b>
$N_2 + e^- = 2N + e^-$	$3.00 \times 10^{24}$	<b>-1.6</b>	<b>113 100</b>
$N_2 + N^+ = N_2^+ + N_g$	$1.00 \times 10^{12}$	<b>0.5</b>	<b>12 200</b>
$N_g + N_g = N_2^+ + e^-$	$1.40 \times 10^{13}$	<b>0.0</b>	<b>67 800</b>
$N_g + N = N + N^+ + e^-$	$2.34 \times 10^{11}$	<b>0.5</b>	<b>120 000</b>
$N_g + N^+ = 2N^+ + e^-$	$2.34 \times 10^{11}$	<b>0.5</b>	<b>120 000</b>
$N_g + e^- = N^+ + 2e^-$	$2.50 \times 10^{16}$	<b>0.0</b>	<b>169 000</b>
$N_g + e^- = N^* + e^-$	$5.56 \times 10^{16}$	<b>0.0</b>	<b>121 000</b>
$N^* + e^- = N^+ + 2e^-$	$4.11 \times 10^{17}$	<b>0.0</b>	<b>48 900</b>

Rates in the form  $k_f = AT^B \exp(-E/T)$ ;  $T = T_e$  in electron impact reactions;  $N = N_g + N^*$ .

**Reactions of dissociation for air [101]**

<b>Reaction</b>	<b>M</b>	<b><math>k_0, \text{cm}^3/\text{mol} \cdot \text{s}</math></b>
$N_2 + M \rightarrow N + N + M$	<b>N, N<sup>+</sup>, O, O<sup>+</sup></b> <b>N2, N2+, O2, O2+, NO, NO+</b> <b>E</b>	$3.0 \times 10^{22} \cdot T^{-1.6} \cdot \exp(-113200/T)$ $7.0 \times 10^{21} \cdot T^{-1.6} \cdot \exp(-113200/T)$ $3.0 \times 10^{24} \cdot T^{-1.6} \cdot \exp(-113100/T)$
$O_2 + M \rightarrow O + O + M$	<b>N, N<sup>+</sup>, O, O<sup>+</sup></b> <b>N2, N2+, O2, O2+, NO, NO+</b>	$1.0 \times 10^{22} \cdot T^{-1.5} \cdot \exp(-59500/T)$ $2.0 \times 10^{21} \cdot T^{-1.5} \cdot \exp(-59500/T)$
$NO + M \rightarrow N + O + M$	<b>N, N<sup>+</sup>, O, O<sup>+</sup>, NO</b> <b>N2, N2+, O2, O2+, NO+</b>	$1.1 \times 10^{17} \cdot T^0 \cdot \exp(-75500/T)$ $5.00 \times 10^{15} \cdot T^0 \cdot \exp(-75500/T)$

**Reactions of ionization for air [101]**

<b>Reaction</b>	<b><math>k_{f,r}, \text{cm}^3/\text{mol} \cdot \text{s}</math></b>
$O + e \rightarrow O^+ + e + e$	$k_f = 6.35 \times 10^{15} \cdot T_e^0 \cdot \exp(-106200/T_e)$
$N + e \rightarrow N^+ + e + e$	$k_f = 5.08 \times 10^{16} \cdot T_e^0 \cdot \exp(-121000/T_e)$

$N+N \rightarrow N^+ + e + N$	$k_f = 2.34 \times 10^{11} \cdot T^{0.5} \cdot \exp(-120000/T)$
$N+N^+ \rightarrow N^+ + e + N^+$	$k_f = 2.34 \times 10^{11} \cdot T^{0.5} \cdot \exp(-120000/T)$
$O+O \rightarrow O_2^+ + e$	$k_f = 1.10 \times 10^{13} \cdot T^0 \cdot \exp(-80600/T)$
$N+O \rightarrow NO^+ + e$	$k_f = 5.30 \times 10^{12} \cdot T^0 \cdot \exp(-31900/T)$
$N+N \rightarrow N_2^+ + e$	$k_f = 2.00 \times 10^{13} \cdot T^0 \cdot \exp(-67500/T)$

**Charge-exchange reactions for air [101]**

Reaction	$k_f, \text{cm}^3/\text{mol} \cdot \text{s}$
$O_2^+ + N_2 \rightarrow O_2 + N_2^+$	$9.9 \times 10^{12} \cdot T^0 \cdot \exp(-40700/T)$
$O_2^+ + N \rightarrow O_2 + N^+$	$8.7 \times 10^{13} \cdot T_e^{0.14} \cdot \exp(-28600/T)$
$NO^+ + O \rightarrow N^+ + O_2$	$1.00 \times 10^{12} \cdot T^{0.5} \exp(-77200/T)$
$N^+ + N_2 \rightarrow N_2^+ + N$	$1.00 \times 10^{12} \cdot T^{0.5} \exp(-12200/T)$
$O^+ + NO \rightarrow N^+ + O_2$	$1.4 \times 10^5 \cdot T^{1.9} \cdot \exp(-26600/T)$
$NO^+ + N \rightarrow O^+ + N_2$	$3.40 \times 10^{13} \cdot T^{-1.08} \exp(-12800/T)$
$O^+ + N_2 \rightarrow O + N_2^+$	$9.0 \times 10^{11} \cdot T^{0.36} \cdot \exp(-22800/T)$
$NO^+ + N \rightarrow O + N_2^+$	$7.2 \times 10^{13} \cdot T^0 \exp(-35500/T)$
$O_2^+ + O \rightarrow O^+ + O_2$	$4.00 \times 10^{12} \cdot T^{-0.09} \cdot \exp(-18000/T)$
$NO^+ + O_2 \rightarrow NO + O_2^+$	$2.30 \times 10^{13} \cdot T^{0.41} \cdot \exp(-32600/T)$
$NO^+ + O \rightarrow O_2^+ + N$	$7.20 \times 10^{12} \cdot T^{0.29} \exp(-48600/T)$
$NO^+ + O \rightarrow O_2 + N^+$	$1.00 \times 10^{12} \cdot T^{0.5} \cdot \exp(-77200/T)$

**Chemical bimolecular reactions [101]**

Reaction	$k_f, \text{cm}^3/\text{mol} \cdot \text{s}$
$NO + O \rightarrow O_2 + N$	$8.40 \times 10^{12} \cdot T^0 \exp(-19450/T)$
$N_2 + O \rightarrow NO + N$	$6.40 \times 10^{17} \cdot T^{-1.0} \cdot \exp(-38400/T)$

**Table RD.13: Rates of activation and deactivation of electronic excited states of diatomic molecules [91]**

No. of process	Process	A	n	E, K	A
1	$CN(X^2\Sigma^+) + M_1 \rightarrow CN(B^2\Sigma^+) + M_1$	$2.24 \times 10^{10}$	0.5	37000	$1.8 \times 10^{11}$
2	$CN(X^2\Sigma^+) + e \rightarrow CN(B^2\Sigma^+) + e$	$7.8 \times 10^{13}$	0.5	37000	$6.24 \times 10^{14}$
3	$CN(X^2\Sigma^+) + M_1 \rightarrow CN(A^3\Pi) + M_1$	$1.5 \times 10^{10}$	0.5	13300	$1.5 \times 10^{11}$

<b>4</b>	$\text{CN}(X^2\Sigma^+) + e \rightarrow \text{CN}(A^2\Pi) + e$	$6.0 \times 10^{13}$	<b>0.5</b>	<b>13300</b>	$6.0 \times 10^{14}$
<b>5</b>	$\text{CO}(X^1\Sigma^+) + M \rightarrow \text{CO}(A^1\Pi) + M$	$4.5 \times 10^2$	<b>2.86</b>	<b>93000</b>	
<b>6</b>	$\text{CO}(X^1\Sigma^+) + M \rightarrow \text{CO}(A^1\Sigma^+) + M$	$2.2 \times 10^2$	<b>2.86</b>	<b>125000</b>	
<b>7</b>	$\text{CO}(X^1\Sigma^+) + M \rightarrow \text{CO}(b^3\Sigma^+) + M$	$10^{14}$	<b>0.5</b>	<b>120900</b>	
<b>8</b>	$\text{CO}(X^1\Sigma^+) + e \rightarrow \text{CN}(A^2\Sigma^2) + e$	$2.0 \times 10^{14}$	<b>0.5</b>	<b>66000</b>	
<b>9</b>	$\text{C}_2(X^1\Sigma_g^+) + e \rightarrow \text{C}_2(d^3\Pi_g) + e$	$7.82 \times 10^{15}$	<b>0.15</b>	<b>28807</b>	
<b>10</b>	$\text{C}_2(X^2\Sigma_g^+) + M_1 \rightarrow \text{C}_2(d^3\Pi_g) + M_1$	$1.95 \times 10^{12}$	<b>0.15</b>	<b>28807</b>	

**Radiative life-times of electronic states in [ 91]**

<b>Process</b>	<b><math>\tau_{mn}</math>, s</b>	<b>Process</b>	<b><math>\tau_{mn}</math>, s</b>
$\text{CN}(B^2\Sigma^+) \rightarrow \text{CN}(A^2\Pi) + h\nu$	$6.25 \times 10^{-8}$	$\text{CO}(B^1\Sigma^+) \rightarrow \text{CO}(A^1\Pi) + h\nu$	$2.37 \times 10^{-8}$
$\text{CN}(B^2\Sigma^+) \rightarrow \text{CN}(A^2\Sigma^+) + h\nu$	$6.25 \times 10^{-8}$	$\text{CO}(B^1\Sigma^+) \rightarrow \text{CO}(X^1\Sigma^+) + h\nu$	$2.37 \times 10^{-8}$
$\text{CN}(A^2\Pi) \rightarrow \text{CN}(X^2\Sigma^+) + h\nu$	$8.0 \times 10^{-6}$	$\text{CO}(b^3\Sigma^+) \rightarrow \text{CO}(a^3\Pi) + h\nu$	$5.62 \times 10^{-8}$
$\text{C}_2(d^3\Pi_g) \rightarrow \text{C}_2(a^3\Pi_u) + h\nu$	$1.07 \times 10^{-7}$	$\text{CO}^+(B^2\Sigma^+) \rightarrow \text{CO}^+(X^2\Sigma^+) + h\nu$	$5.2 \times 10^{-8}$
$\text{CO}(A^1\Pi) \rightarrow \text{CO}(X^1\Sigma^+) + h\nu$	$1.0 \times 10^{-8}$	$\text{CO}^+(B^2\Sigma^+) \rightarrow \text{CO}^+(A^2\Pi) + h\nu$	$5.2 \times 10^{-8}$

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